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Perturbation Theory Calculation of the Pressure for an Electron-Ion System

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Abstract

By means of finite-temperature, many-body perturbation theory we derive through order e^4 the corrections to an ideal Fermi gas plus an ideal Maxwell-Boltzmann gas of ions. This computation is carried out for general values of the de Broglie density. The behavior of these coefficients is reported, and their implications for the ionization profile at low densities are described.

Key words: equations of state; dense plasmas; finite-temperature, quantum, perturbation theory; Padé approximants
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1 INTRODUCTION AND SUMMARY

There has been, and there continues to be, strong interest in the computation of as much as possible in the way of exact results for the equation of state of matter under extreme conditions. In stellar interiors, in plasma fusion, and in some other applications, the familiar regime of solids, liquids and gases ceases to be germane. Rather the fluid state in which liquids and gases are not distinguishable is what is important. In this paper we will be concerned with a hot and/or dense system of electrons and ions. For a long time, the mainstay [1–4] of the theory of the equation of state at higher temperatures and densities has been the Thomas-Fermi or the Thomas-Fermi-Dirac theory. These theories correctly reduce to the electron ideal gas [5] at sufficiently high temperature, but as we [6] pointed out previously, even the first deviation from this limit is incorrectly given by these theories. In this paper we report the computation of the expansion in powers of the charge on the electron e of corrections to the ideal Fermi gas, or "hot-curve" limit. The method which we employ is the finite temperature, Matsubara, many-body, perturbation theory [7]. We carry this theory through order e^4. As the thermodynamic functions in the ideal Fermi gas case are functions of the de Broglie density, the coefficients that we obtain in this expansion are likewise functions of the de Broglie density. The de Broglie density ζ is basically the density times the cube of the thermal wave length and is defined by (3.1). Preliminary reports [8–10] of this work have been given and we draw on them, correcting where necessary a number of infelicities. A great many things can be deduced from these expansion coefficients, however the main point of this paper is to report their computation. We do give a short report on the high-temperature behavior of the low density ionization profile, as an example of one of the things that can be learned.

In the second section we cover the necessary perturbation theory for our project. Here the values of the various diagrams are obtained in terms of the electron and the ion fugacities. In the third section we derive the expansion of these coefficients in powers of the fugacities. Thermodynamics tells us what the equations are that relate the fugacities to thermodynamically observable quantities. In the fourth section we derive these equations and solve them to the necessary order in e. Following Baker and Johnson [5], we revert the equation for the de Broglie density in powers of the fugacity to give the fugacity in powers of the de Broglie density. By back substitution, we may then re-express all the other expansions which are in powers of the fugacity as expansions in powers of the de Broglie density. Our results are given in (4.14) and the coefficients for that equation are defined in (4.15-18). In order to be of practical use, it is desirable to obtain representations which are valid for all positive real de Broglie densities. In the fifth section, based on the Padé method [11], we derive compact representations of the various required functions. These (with one exception) are accurate to within about 0.1 percent. In the sixth section, we examine the behavior of the various coefficients. Finally, in the seventh section we discuss the low-density behavior of the ionization profile in the high-temperature region. Strictly speaking, by the ionization profile, we mean the density of singly, doubly, *etc.* ionized atoms and the density of free electrons. These concepts only make sense when individual atoms can be identified. When for example, the density is sufficiently high, the system more closely resembles a soup of electrons and ions and the concept of an atom looses its meaning. In this study, we confine our attention to the density of the electrons and the dilute region where the concept of an atom makes sense.

Comparison could be made with the results of the much studied restrictive primitive model (See for example, [12] and [13] and most particularly, the numerous references therein. Particular attention is drawn to [14] for comparison purposes. We will however defer these studies to the future. There are also a number of other approaches with which cross comparison should be enlightening.

2 PERTURBATION THEORY

One goal in this paper is to compute, for general de Broglie density, the perturbations to the ideal Fermi gas pressure caused by the electrostatic interactions between electrons and ions. We will treat the electrons as charged Fermions, but will treat the ions as Maxwell-Boltzmann particles. The treatment of the ions could be improved, if required. We start with the electrically neutral Hamiltonian,

$$H = \sum_{i=1}^{ZN} \frac{p_i^2}{2m} + \sum_{j=1}^{N} \frac{P_j^2}{2M} + \sum_{i<j}^{ZN} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i}^{ZN} \sum_{j}^{N} \frac{Ze^2}{|\vec{r}_i - \vec{R}_j|} + \sum_{i<j}^{N} \frac{Z^2 e^2}{|\vec{R}_i - \vec{R}_j|}, \tag{2.1}$$

where $\vec{r}$, $\vec{p}$ are the position and momentum for the electrons and $\vec{R}$, $\vec{P}$ are for the ions of charge Z. To treat our problem we employ finite-temperature perturbation theory (Matsubara [7]). It is known that when this theory is applied to the Coulomb potential, that some of the terms diverge in a rather serious manner. Gell-Mann and Brueckner [15] however have shown that if all the so-called "ring-diagrams" are summed up before the integration over the momentum transfer is performed, then the result is finite, but the order in the coupling constant e^2 is changed. We will discuss this point in more detail below. Bedenov [16] briefly describes his investigation of our case for a degenerate plasma. A fuller description is given by Abrikosov *et al.* [17]

To begin we note that the thermodynamic potential $p\Omega$, where p is the pressure and Ω is the volume, (See, for example, pp. 68-71 and 105-107 of Landau and Lifshitz [18]) is given by $-kT \log \mathcal{Q}$ where k is Boltzmann's constant, T is the absolute temperature and $\mathcal{Q}$ is the partition function from the grand canonical ensemble. In terms of other thermodynamic quantities $p\Omega = TS + \mu N - U$, where S is the entropy, μ is the Gibbs free energy, or thermodynamic potential, per particle, N is the number of particles, and U is the internal energy. The perturbation series for the pressure is related to that for the energy by the observation that,

$$\frac{\partial(-kT \log \mathcal{Q})}{\partial e^2} = e^{-2} \langle V \rangle, \tag{2.2}$$

where V is the interaction potential, *i.e.* everything proportional to e^2 in (2.1). Thus,

$$p\Omega = \int_0^{e^2} e^{-2} \langle V \rangle \, de^2 + p_0 \Omega, \tag{2.3}$$

relates the series for the energy and that for the pressure. Note that, of course, the wave function changes as e increases in the integral. The quantity p_0 is the ideal Fermi gas pressure given by (3.2).

The finite-temperature perturbation series is conveniently described in the wave-number space representation. The wave-number representation for the interaction potential is

$$V(\vec{r}) = \frac{e^2}{r} \mapsto \tilde{v}(\vec{q}) = \frac{4\pi e^2}{q^2}. \tag{2.4}$$

The rules for the perturbation series for the interaction energy which insure that the proper quantum mechanical expectation values are taken are briefly: First draw the Goldstone type diagrams which are associated with the various terms in the perturbation series. We in fact use the type of diagrams discussed by Baker [19]. Here there are no lines entering on the left nor leaving on the right. Label every line in such a way that the wave-number is conserved at every vertex. Associate a frequency with each independent wave-number. The frequencies must also obey a conservation rule at every vertex. The frequencies on every Fermion line are odd ($\omega_n = (2n+1)\pi kT$) and those with every Boson line must be even ($\omega_n = 2\pi nkT$). Now with each fermion line (particle or hole) associate a factor of

$$\frac{e^{i\omega_n'\tau}}{i\omega_n' - \epsilon(\vec{p}\,') + \mu}, \tag{2.5}$$

where ω_n' and $\vec{p}\,'$ are the frequency and the wave-number associated with that line. We define,

$$\epsilon(\vec{p}) \equiv \frac{\hbar^2 p^2}{2m}, \tag{2.6}$$

where $\hbar$ is Planck's constant h divided by 2π. With each Boson line (the wavy lines internal to each interaction symbol) associate a factor of $\tilde{v}(\vec{q})$ where $\vec{q}$ is the wave-number associated with that line. Note that if the vertex is not electron-electron, then a factor of Z or Z^2 would also be needed as the case may be, and as it is really momentum that is conserved, account of the masses must be taken. Next examine the diagram of order n vertices and count the number of closed loops l made by the combination of the particle and hole lines. Multiply the term by a factor of

$$\frac{(2s+1)^l(-1)^l(-kT)^{n+1}}{(2\pi)^{3(n+1)}2^n}. \tag{2.7}$$

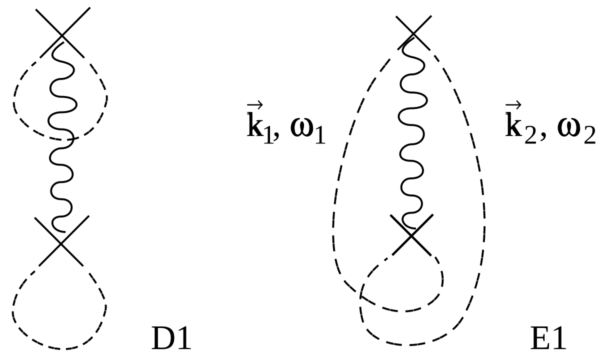

Fig. 1. The diagrams for the first-order interaction in e^2. The wavy lines represent the momentum transfer during an interaction, the dashed lines are Fermion holes, and the solid lines (in subsequent diagrams) represent Fermions.

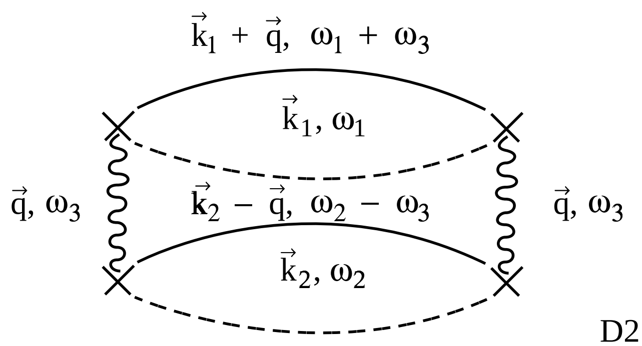

Fig. 2. The second-order direct-interaction diagram. See the caption of Fig. 1 for the line descriptions.

Next sum over the independent frequencies, take the limit as $\tau \to 0$, and finally integrate over all the independent wave-numbers. The following identities are useful in doing the frequency sums.

$$
\begin{aligned}
kT \sum_{n=-\infty}^{+\infty} \frac{1}{2n\pi i kT + X} &= \frac{1}{2}\coth\left(\frac{X}{2KT}\right), \\
\lim_{\tau \to 0} kT \sum_{n=-\infty}^{+\infty} \frac{e^{i\tau}}{(2n+1)\pi i kT + X} &= \frac{1}{2}\tanh\left(\frac{X}{2kT}\right) + \frac{1}{2}\mathrm{sgn}(\tau), \qquad (2.8) \\
n(\vec{p}) = \frac{1}{\exp\{[\epsilon(\vec{p}) - \mu]/(kT)\} + 1} &= \frac{1}{2}\left[1 - \tanh\left(\frac{\epsilon(\vec{p}) - \mu}{2kT}\right)\right].
\end{aligned}
$$

Our goal will be to compute the corrections to the pressure to the order of e^4. The first step is to examine all the diagrams up to and including two

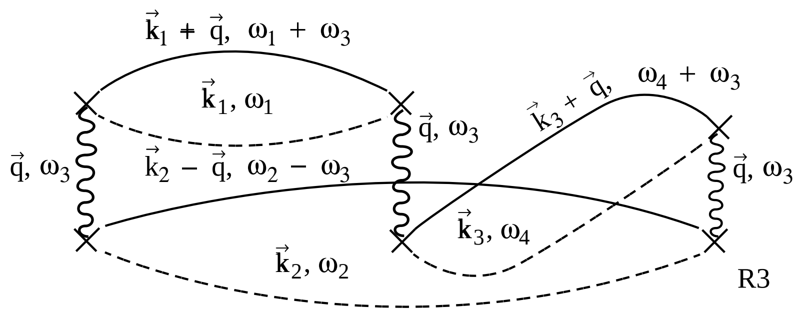

Fig. 3. The third-order ring diagram. See the caption of Fig. 1 for the line descriptions.

interactions. We will, following Abrikosov *et al.* [17], ignore the ion exchange terms as relatively small. The electron-ion exchange terms do not exist as they are not identical particles. In first order in e^2, the direct terms, $D1$ shown in Fig. 1, consisting of the electron-electron, electron-ion and ion-ion terms cancel each other out by electrical neutrality. The first exchange term, $E1$ shown in Fig. 1, by our rules, gives the contribution,

$$p_{E1} = -\frac{4\pi e^2}{(2\pi)^6}\int \frac{d\vec{k}_1\, d\vec{k}_2}{(\vec{k}_1 - \vec{k}_2)^2} n(\vec{k}_1) n(\vec{k}_2), \tag{2.9}$$

which agrees with the results of Abrikosov *et al.* [17]. This result concludes the study of the first-order perturbation theory.

In second order in e^2 there are a number of cases to consider. The first is the so called direct term, $D2$, Fig. 2. We work initially, for ease of exposition, with the electron-electron terms. Since there are two equivalent direct terms, we get,

$$-\frac{2(4\pi e^2)^2(kT)^3}{(2\pi)^9}\sum_{\omega_1,\omega_2,\omega_3}\int\frac{d\vec{k}_1\, d\vec{k}_2\, d\vec{q}}{q^2 q^2}\left[\frac{1}{i\omega_1 - \epsilon(\vec{k}_1) + \mu}\,\frac{1}{i\omega_2 - \epsilon(\vec{k}_2) + \mu}\right.$$
$$\left.\times\frac{1}{i\omega_1 + i\omega_3 - \epsilon(\vec{k}_1 + \vec{q}) + \mu}\,\frac{1}{i\omega_2 - i\omega_3 - \epsilon(\vec{k}_2 - \vec{q}) + \mu}\right], \tag{2.10}$$

where ω_1 and ω_2 are odd and ω_3 is even. The thing to notice is that the integral over $\vec{q}$ diverges as $q \to 0$. The solution to this problem was given by Gell-Mann and Brueckner [15] in the context of the ground-state energy problem. It is to sum up all the "ring diagrams" before doing the integral over the momentum transfer, $\vec{q}$. The Fourier transform trick used by them to sum up these diagrams to all orders is basically incorporated in our formalism, if we are careful to wait until after summing up all orders to sum over ω_3. Doing the sums over ω_1 and ω_2 in (2.10) we get,

$$-\frac{kT}{2(2\pi)^3}\sum_{\omega_3}\int d\vec{q}\left[\frac{8\pi e^2}{q^2}\Xi(\vec{q},\omega_3)\right]^2, \tag{2.11}$$

where

$$\Xi(\vec{q},\omega_3)=\frac{1}{(2\pi)^3}\int\frac{[n(\vec{k})-n(\vec{k}-\vec{q})]\,d\vec{k}}{-i\omega_3+\epsilon(\vec{k})-\epsilon(\vec{k}-\vec{q})}. \tag{2.12}$$

In third order in e^2 there is just one term, Fig. 3, which gives the contribution

$$-\frac{kT}{2(2\pi)^3}\sum_{\omega_3}\int d\vec{q}\left[\frac{8\pi e^2}{q^2}\Xi(\vec{q},\omega_3)\right]^3, \tag{2.13}$$

In higher-orders, there are many "vertex orders" of the same diagram, but by the arguments of Gell-Mann and Brueckner [15], they are represented in our formalism by a single term. The whole series of these most highly divergent terms in the perturbation expansion for $\langle V\rangle$ then formally sums to

$$-\frac{kT}{2(2\pi)^3}\sum_{\omega_3}\int d\vec{q}\left\{\frac{[8\pi e^2\Xi(\vec{q},\omega_3)]^2}{q^2-8\pi e^2\Xi(\vec{q},\omega_3)}\right\}. \tag{2.14}$$

When we convert (2.14) to the series for the $p\Omega$, by (2.3), we get, interchanging the orders of integration,

$$-\frac{kT}{2(2\pi)^3}\sum_{\omega_3}\int d\vec{q}\left\{\ln\left[1-\frac{8\pi e^2}{q^2}\Xi(\vec{q},\omega_3)\right]+\frac{8\pi e^2}{q^2}\Xi(\vec{q},\omega_3)\right\}. \tag{2.15}$$

The next problem is to analyze the leading order behavior in the limit of small e^2. To this end we introduce the dimensionless variable,

$$y^2=\frac{Ze^2}{kTr_b},\quad \Omega=\tfrac{4}{3}\pi r_b^3 N. \tag{2.16}$$

If we re-express the wave number $\vec{q}=y\vec{p}$, then Ξ becomes,

$$\Xi(y\vec{p},\omega_3)=-\frac{1}{(2\pi)^3}\int\frac{d\vec{k}\,\left(\frac{\Delta\epsilon}{4kT}\right)\mathrm{sech}^2\left(\frac{\epsilon(\vec{\mathrm{k}})-\mu}{2\mathrm{kT}}\right)+\mathrm{O}(\mathrm{y}^3)}{-i\omega_3+\Delta\epsilon}, \tag{2.17}$$

where

$$\Delta\epsilon = \hbar^2(2y\vec{p}\cdot\vec{k} - y^2p^2)/(2m), \tag{2.18}$$

and one term in (2.17) of nominal order y^2 is not shown because it vanishes on integration over the angles of $\vec{k}$. In order to do the sum over ω_3, there are two cases to consider. In the first, $\omega_3 = 0$, and

$$\Xi(y\vec{p},0) = -\frac{1}{4kT(2\pi)^3}\int d\vec{k}\,\mathrm{sech}^2\left(\frac{\epsilon(\vec{\mathrm{k}})-\mu}{2\mathrm{kT}}\right), \tag{2.19}$$

which is independent of $\vec{p}$. In the case where $\omega_3 \neq 0$, Ξ is of nominal order y which is already small compared to the $\omega_3 = 0$ case which was of order unity, but again the integration over the angles of $\vec{k}$ reduces the size even further to the order of y^2. Thus we only need to retain the $\omega_3 = 0$ term to give the leading order, plus the next order as well, for the sum of these ring diagrams. When we recognize that integration by parts *etc.* yields,

$$\int_0^\infty \left[\ln\left(1+\frac{1}{k^2}\right) - \frac{1}{k^2}\right] k^2\,dk = -\frac{\pi}{3}, \tag{2.20}$$

we may write that our sum of ring diagrams is

$$-\frac{kT}{(2\pi)^2}\left(\frac{\pi}{3}\right)\left[\frac{e^2}{(2\pi)^2kT}\int d\vec{k}\,\mathrm{sech}^2\left(\frac{\epsilon(\vec{\mathrm{k}})-\mu}{2\mathrm{kT}}\right)\right]^{3/2}, \tag{2.21}$$

which is of order e^3 with an error term of order e^4 as the integration in (2.20) changes the order of the errors from the expected e^5. The divergence in the integration over $\vec{q}$ has been converted into a lower order in the expansion parameter.

The work to include the ion terms is just the same, except that e^2 is multiplied by $-Z$ for the electron-ion interactions and by Z^2 for the ion-ion interactions, the ions are being treated as spinless, and the ions have a Maxwell-Boltzmann distribution rather than a Fermi-Dirac one. The proper change is to make Ξ the sum of the electron (2.12), plus Z^2 times the ion function, which substitutes,

$$n_{\mathrm{ion}}(\vec{k}) = \frac{1}{2}\exp\{[\mu - \epsilon(\vec{k})]/(kT)\}, \tag{2.22}$$

for $n(\vec{k})$. The factor $\frac{1}{2}$ is to take account of no ion spin. Thus (2.21) becomes, to take account of all the interactions,

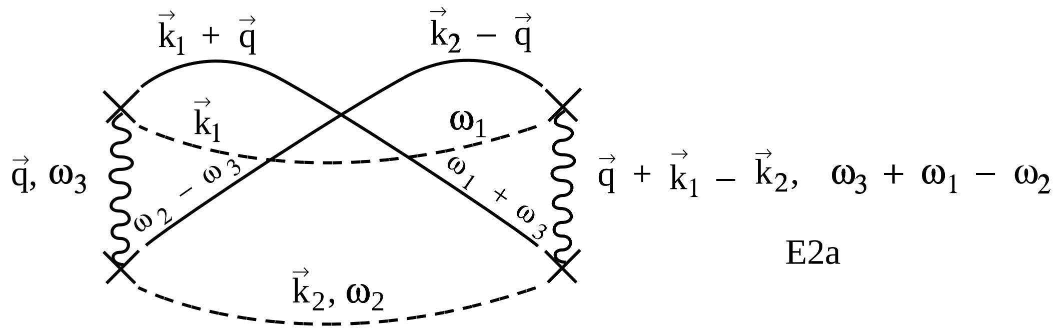

Fig. 4. The second-order exchange-interaction diagram. See the caption of Fig. 1 for the line descriptions.

$$p_{DH} = -\frac{kT}{(2\pi)^2}\left(\frac{\pi}{3}\right)\left[\frac{4\pi Z^2 N e^2}{kT\Omega} + \frac{e^2}{(2\pi)^2 kT}\int d\vec{k}\,\mathrm{sech}^2\left(\frac{\epsilon(\vec{\mathrm{k}}) - \mu}{2\mathrm{kT}}\right)\right]^{3/2}, \tag{2.23}$$

since the integral over the resulting function in the ion case is easily expressed in terms of the density normalization. This finishes the study of the terms of order e^3, or the Debye-Hückel term.

We now consider the calculation of the terms of order e^4 which we call the second exchange correction. We do not know of previous work on this term. The first contribution $E2a$ is the exchange, Fig. 4, of the the direct term shown in Fig. 2. Following the rules as expounded above, we obtain for electron-electron exchange, by reducing the integrand to dimensionless form,

$$\begin{aligned} p_{E2a} = {} & \frac{(4\pi e^2)^2}{2^5 kT(2\pi)^9}\left(\frac{2mkT}{\hbar^2}\right)^{5/2}\int \frac{d\vec{k}_1\, d\vec{k}_2\, d\vec{q}}{q^2(\vec{q}+\vec{k}_1-\vec{k}_2)^2}\,\frac{\sinh(\vec{q}\cdot(\vec{q}+\vec{k}_1-\vec{k}_2))}{\vec{q}\cdot(\vec{q}+\vec{k}_1-\vec{k}_2)} \\ & \times\left[\cosh\left(\frac{(\vec{q}+\vec{k}_1)^2}{2} - \frac{\mu}{2kT}\right)\cosh\left(\frac{k_1^2}{2} - \frac{\mu}{2kT}\right)\cosh\left(\frac{(\vec{k}_2-\vec{q})^2}{2} - \frac{\mu}{2kT}\right)\right. \\ & \left.\times\cosh\left(\frac{k_2^2}{2} - \frac{\mu}{2kT}\right)\right]^{-1} \end{aligned} \tag{2.24}$$

where use has been made of the standard identities,

$$\coth x + \coth y = \frac{\sinh(x+y)}{\sinh x \sinh y}, \quad \tanh x + \tanh y = \frac{\sinh(x+y)}{\cosh x \cosh y}, \tag{2.25}$$

to obtain this form.

Next, there occurs to this order in perturbation theory one term which does

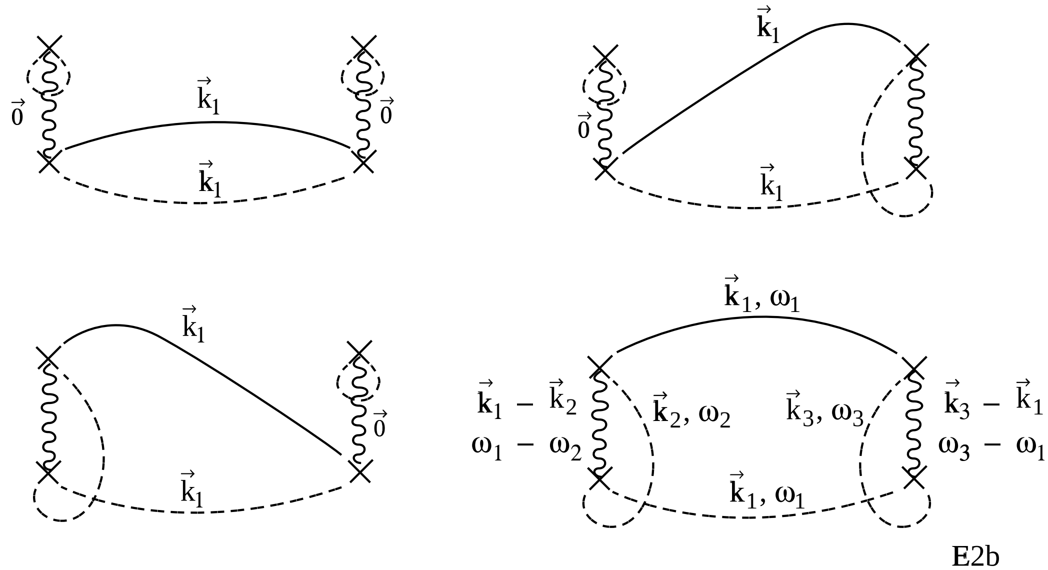

Fig. 5. The second-order "forbidden diagram" and its exchange variants. See the caption of Fig. 1 for the line descriptions.

not occur in the ground state energy expansion, plus its three exchange variants. They are shown in Fig. 5. The reason that they do not appear in the ground state energy perturbation theory is that, contrary to finite-temperature perturbation theory, in that theory there can not be simultaneously a hole and a particle with the same momentum. In finite-temperature theory, we are dealing with an ensemble and hence can have, on the average, fractional occupation of a state, and hence this case is not forbidden. In the first three terms shown in Fig. 5 there is at least one interaction in which zero momentum is exchanged. All three of these cases cancel among the corresponding electron-electron, electron-ion and ion-ion terms by electrical neutrality. In the final case, whose contribution we call $E2b$, there is exchange at both vertices. The contribution here for electron-electron exchange can be worked out by taking the $\partial/\partial X$ of the second identity of (2.8) to get the frequency sum where one of the denominators appears squared. Again reducing the integrand to dimensionless form, we obtain,

$$p_{E2b} = -\frac{(4\pi e^2)^2}{2^3 kT(2\pi)^9}\left(\frac{2mkT}{\hbar^2}\right)^{5/2}\int \frac{d\vec{k}_1\, d\vec{k}_2\, d\vec{k}_3}{(\vec{k}_2-\vec{k}_1)^2(\vec{k}_1-\vec{k}_3)^2} \times \frac{\operatorname{sech}^2\left(\frac{1}{2}\mathrm{k}_1^2 - \frac{\mu}{2\mathrm{kT}}\right)}{\left[1+\exp\left(k_2^2-\frac{\mu}{kT}\right)\right]\left[1+\exp\left(k_3^2-\frac{\mu}{kT}\right)\right]}. \tag{2.26}$$

Again, as in the first exchange correction, we ignore here, and in $E2a$, the ion-ion exchange as being relatively small.

Finally in order to compute the e^4 order term which is given by our sum of the ring diagrams, it is necessary to analyze the difference between the whole term and the leading order e^3 term. We may conveniently write this difference as,

$$
\begin{aligned}
&-\frac{kT}{2(2\pi)^3}\sum_{\omega_3}\int d\vec{q}\,\Bigg\{\ln\left[1-\frac{8\pi e^2}{q^2}[\Xi(\vec{q},\omega_3)+Z^2\Xi_{\rm ion}(\vec{q},\omega_3)]\right]\\
&\qquad\qquad+\frac{8\pi e^2}{q^2}[\Xi(\vec{q},\omega_3)+Z^2\Xi_{\rm ion}(\vec{q},\omega_3)]\Bigg\}\\
&\quad+\frac{kT}{2(2\pi)^3}\int d\vec{q}\,\Bigg\{\ln\left[1-\frac{8\pi e^2}{q^2}[\Xi(\vec{0},0)+Z^2\Xi_{\rm ion}(\vec{0},0)]\right]\\
&\qquad\qquad+\frac{8\pi e^2}{q^2}[\Xi(\vec{0},0)+Z^2\Xi_{\rm ion}(\vec{0},0)]\Bigg\}.
\end{aligned}
\tag{2.27}
$$

If we expand this expression for small e^2 we obtain, for the e^4 term,

$$
\begin{aligned}
p_{DH4}=\frac{kT}{4(2\pi)^3}\sum_{\omega_3}\int d\vec{q}\,&\Bigg\{\left[\frac{8\pi e^2}{q^2}[\Xi(\vec{q},\omega_3)+Z^2\Xi_{\rm ion}(\vec{q},\omega_3)]\right]^2\\
&-\delta_{0,\omega_3}\left[\frac{8\pi e^2}{q^2}[\Xi(\vec{0},0)+Z^2\Xi_{\rm ion}(\vec{0},0)]\right]^2\Bigg\},
\end{aligned}
\tag{2.28}
$$

which, as we will see, yields a finite coefficient for e^4. The Kronecker delta is denoted by $\delta_{n,m}$. The next correction is expected to be of the order of $o(e^4)$.

At this point it is useful to note a general property of Ξ and $\Xi_{\rm ion}$. As the energy $\epsilon(\vec{k})=\epsilon(-\vec{k})$, the variable change $\vec{\kappa}=\vec{q}-\vec{k}$ interchanges the two terms n in the numerator and the two terms ϵ in the denominator of (2.12). Thus $\Xi(\vec{q},\omega_3)=\Xi(\vec{q},-\omega_3)=\Xi^*(\vec{q},\omega_3)$ and likewise $\Xi_{\rm ion}(\vec{q},\omega_3)=\Xi_{\rm ion}(\vec{q},-\omega_3)=\Xi^*_{\rm ion}(\vec{q},\omega_3)$. Hence the whole term is just twice the real part of the term using only the first n term in the numerator. Also the terms for $\omega_3<0$ are equal to those for $\omega_3>0$. Thus we need only treat the case of $\omega_3\geq 0$.

It is useful next to employ the identity,

$$
\frac{kT}{-i\omega_3+\epsilon(\vec{k})-\epsilon(\vec{k}-\vec{q})}=i\int_0^\infty dt\,\exp\{-t[\omega_3+i\epsilon(\vec{k})-i\epsilon(\vec{k}-\vec{q})]/(kT)\}.
\tag{2.29}
$$

Thus we get,

$$\Xi(\vec{q},\omega_3) \tag{2.30}$$
$$= \frac{2}{(2\pi)^3 kT}\Re\left\{ i\int_0^\infty dt \int d\vec{k}\, n(\vec{k}) \exp\{-t[\omega_3 + i\epsilon(\vec{k}) - i\epsilon(\vec{k}-\vec{q})]/(kT)\}\right\},$$

and

$$\Xi_{\rm ion}(\vec{q},\omega_3) = \frac{2}{(2\pi)^3 kT} \tag{2.31}$$
$$\times\Re\left\{ i\int_0^\infty dt \int d\vec{k}\, n_{\rm ion}(\vec{k}) \exp\{-t[\omega_3 + i\epsilon_{\rm ion}(\vec{k}) - i\epsilon_{\rm ion}(\vec{k}-\vec{q})]/(kT)\}\right\}.$$

In the ion case the density function (2.22) is of Gaussian form which permits the integration over $\vec{k}$ in (2.31) to be evaluated as,

$$\Xi_{\rm ion}(\vec{q},\omega_3) = -\frac{z_{\rm ion}}{kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}} \int_0^\infty dt\ \exp\left(-\nu^2 t^2 - \frac{\omega_3}{kT}t\right)\sin(\nu^2 t), \tag{2.32}$$

where

$$\vec{q} = \left(\frac{2MkT}{\hbar^2}\right)^{\frac{1}{2}}\vec{\nu}, \qquad z_{\rm ion} = \exp[\mu_{\rm ion}/(kT)]. \tag{2.33}$$

The results for the electron case are more complex and are best deferred to the next section where we discuss the expansion in powers of the fugacity.

3 FUGACITY EXPANSION OF THE COEFFICIENTS

The ideal electron gas thermodynamics are all expressible in terms of the de Broglie density,

$$\zeta = \frac{ZN}{2\Omega}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}, \tag{3.1}$$

For example

$$\frac{p_{\rm ideal}\Omega}{ZNkT} \equiv g_0(\zeta) \tag{3.2}$$

The value of the ideal Fermi gas function $g_0(\zeta)$ is well known and is given by (See for example Huang [20])

$$g_0(\zeta) = \frac{2I_{\frac{3}{2}}(z)}{3I_{\frac{1}{2}}(z)}, \tag{3.3}$$

where $z = \exp(\mu/kT)$ is the fugacity and is related to ζ by

$$\zeta = \frac{2}{\sqrt{\pi}} I_{\frac{1}{2}}(z), \tag{3.4}$$

and

$$I_n(z) = \int_0^\infty \frac{zy^n e^{-y}\, dy}{1 + ze^{-y}}. \tag{3.5}$$

The expansions of both ζ and $g_0(z)$ in powers of the fugacity z are also well known and easily derivable from the straightforward expansions

$$I_n(z) = \Gamma(n+1) \sum_{j=1}^{\infty} \frac{(-1)^{j+1} z^j}{j^{n+1}}, \quad n > -1. \tag{3.6}$$

The goal of this section is to expand all the g_j's in series in the fugacity. In the next section we use the results of Baker and Johnson [5] who have reverted the series for $\zeta(z)$ to give the series for the fugacity in powers of the de Broglie density $z(\zeta)$. This method will permit the expression of all the g_j's as series expansions in powers of the de Broglie density. Baker and Johnson [5] give the first 36 terms of the expansion for $g_0(\zeta)$ and 37 terms for $z(\zeta)$. This computation required the retention of a great many decimal places because it is numerically very ill-conditioned.

The deduction of the series for the first exchange correction $g_2(\zeta)$ may be reduced to previous work (Baker and Johnson [6]). If in (2.9) we make the change of variables, $y_i = \hbar^2 k_i^2/(2mkT)$ for $i = 1, 2$ and then integrate over the angles we get,

$$\begin{aligned} p_{E1} &= -\frac{4\pi e^2}{(2\pi)^6} 2\pi^2 \left(\frac{2mkT}{\hbar^2}\right)^2 \int_0^\infty \int_0^\infty \frac{\ln\left|\dfrac{\sqrt{y_1}+\sqrt{y_2}}{\sqrt{y_1}-\sqrt{y_2}}\right|}{(\mathrm{e}^{-y_1} z^{-1} + 1)(\mathrm{e}^{-y_2} z^{-1} + 1)}\, dy_1\, dy_2 \\ &= -\frac{4\pi e^2}{(2\pi)^6} 2\pi^2 \left(\frac{2mkT}{\hbar^2}\right)^2 \hat{X}(z) = -\frac{8\pi e^2 m^2 (kT)^2}{h^4} \hat{X}(z), \end{aligned} \tag{3.7}$$

where $\hat{X}(z)$ agrees with that of (7.2) of Baker and Johnson [6]. They give the result,

$$\hat{X}(z) = \pi \sum_{n_1,n_2=1}^{\infty} \frac{(-z)^{n_1+n_2}}{\sqrt{n_1 n_2}(n_1+n_2)}. \tag{3.8}$$

In the Debye-Hückel pressure (2.23) we have the integral,

$$\begin{aligned}
\int d\vec{k}\, \mathrm{sech}^2\left(\frac{\epsilon(\vec{\mathrm{k}})-\mu}{2\mathrm{kT}}\right) &= 8\pi \left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{z y^{\frac{1}{2}}\, \mathrm{e}^{-y}\, dy}{(1+ze^{-y})^2} \\
&= 8\pi\Gamma(\frac{3}{2}) \left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}} \sum_{j=1}^{\infty} \frac{(-1)^{j+1} z^j}{j^{\frac{1}{2}}} \\
&= 4\pi \left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}} I_{-\frac{1}{2}}(z)
\end{aligned} \tag{3.9}$$

In p_{E2a} (2.24) there appears the integral,

$$\begin{aligned}
&\int \frac{d\vec{k}_1\, d\vec{k}_2\, d\vec{q}}{q^2(\vec{q}+\vec{k}_1-\vec{k}_2)^2} \frac{\sinh(\vec{q}\cdot(\vec{q}+\vec{k}_1-\vec{k}_2))}{\vec{q}\cdot(\vec{q}+\vec{k}_1-\vec{k}_2)} \Bigg[\cosh\left(\frac{(\vec{q}+\vec{k}_1)^2}{2} - \frac{\mu}{2kT}\right) \\
&\times \cosh\left(\frac{k_1^2}{2} - \frac{\mu}{2kT}\right) \cosh\left(\frac{(\vec{k}_2-\vec{q})^2}{2} - \frac{\mu}{2kT}\right) \cosh\left(\frac{k_2^2}{2} - \frac{\mu}{2kT}\right)\Bigg]^{-1}
\end{aligned} \tag{3.10}$$

which using the notation $\eta = \log z = \mu/(kT)$ we can rewrite (3.10) as,

$$\begin{aligned}
&2^3 \int \frac{d\vec{k}_1\, d\vec{k}_2\, d\vec{q}}{q^2(\vec{q}+\vec{k}_1-\vec{k}_2)^2} \int_{-1}^{1} d\lambda\, \exp[\lambda\vec{q}\cdot(\vec{q}+\vec{k}_1-\vec{k}_2)] \\
&\times \frac{\exp[2\eta - q^2 - \vec{q}\cdot(\vec{k}_1-\vec{k}_2) - k_1^2 - k_2^2]}{(1+e^{\eta-(\vec{q}+\vec{k}_1)^2})(1+e^{\eta-k_1^2})(1+e^{\eta-(\vec{q}-\vec{k}_2)^2})(1+e^{\eta-k_2^2})},
\end{aligned} \tag{3.11}$$

where we have artificially introduced the integral over λ for later convenience. Next let us make the change of variables, $\vec{k}_3 = \vec{k}_2 - \vec{k}_1 - \vec{q}$. We now expand the denominator in powers of z as we have done before, and we obtain,

$$\begin{aligned}
&2^3 \sum_{j_1,j_2,j_3,j_4=0}^{\infty} (-1)^{j_1+j_2+j_3+j_4} \int \frac{d\vec{q}\, d\vec{k}_1\, d\vec{k}_3}{q^2 k_3^2} \int_{-1}^{1} d\lambda\, \exp[(2+j_1+j_2+j_3+j_4)\eta \\
&-2k_1^2 - k_3^2 - q^2 - 2\vec{q}\cdot\vec{k}_1 - 2\vec{k}_1\cdot\vec{k}_3 - (1+\lambda)\vec{q}\cdot\vec{k}_3 - j_1(\vec{q}+\vec{k}_1)^2 - j_2 k_1^2
\end{aligned}$$

$$-j_3(\vec{k}_1+\vec{k}_3)^2 - j_4(\vec{k}_1+\vec{k}_3+\vec{q})^2] \tag{3.12}$$

If we now look at the integration over $\vec{k}_1$, we may do it by completing the square in the exponent, and integrating over the Cartesian coordinates. The step yields,

$$\begin{aligned}
&2^3\pi^{\frac{3}{2}} \sum_{j_1,j_2,j_3,j_4=0}^{\infty} \frac{(-1)^{j_1+j_2+j_3+j_4}}{(2+j_1+j_2+j_3+j_4)^{\frac{3}{2}}} \int \frac{d\vec{q}\,d\vec{k}_3}{q^2k_3^2} \int_{-1}^{1} d\lambda \\
&\times \exp\{(2+j_1+j_2+j_3+j_4)\eta - [(1+j_1+j_2)(1+j_3+j_4)k_3^2 \\
&+((2+j_1+j_2+j_3+j_4)(1+2j_4) - 2(1+j_1+j_4)(1+j_3+j_4) \\
&\qquad +\lambda(2+j_1+j_2+j_3+j_4))\vec{q}\cdot\vec{k}_3 \\
&\quad +(1+j_1+j_4)(1+j_2+j_3)q^2]/(2+j_1+j_2+j_3+j_4)\} \quad .
\end{aligned} \tag{3.13}$$

The next step is to do the integrals over all the angles except that between $\vec{q}$ and $\vec{k}_1$, whose cosine we denote as τ. Then, doing the integral over amplitudes by the standard method for a quadratic form in the exponent, we get,

$$\begin{aligned}
&2^4\pi^{\frac{9}{2}} \sum_{j_1,j_2,j_3,j_4=0}^{\infty} \frac{(-1)^{j_1+j_2+j_3+j_4}}{\sqrt{2+j_1+j_2+j_3+j_4}} \int_{-1}^{1} d\lambda\ \exp[(2+j_1+j_2+j_3+j_4)\eta] \\
&\qquad\qquad \times \int_{-1}^{1} \frac{d\tau}{\sqrt{AC-B^2\tau^2}},
\end{aligned} \tag{3.14}$$

where

$$\begin{aligned}
AC &= (1+j_1+j_2)(1+j_3+j_4)(1+j_1+j_4)(1+j_2+j_3) \\
B &= a+b\lambda \\
a &= (2+j_1+j_2+j_3+j_4)(\tfrac{1}{2}+j_4) - (1+j_1+j_4)(1+j_3+j_4) \\
b &= \tfrac{1}{2}(2+j_1+j_2+j_3+j_4)
\end{aligned} \tag{3.15}$$

The integral over τ is elementary and yields,

$$\begin{aligned}
&2^5\pi^{\frac{9}{2}}\hat{T}(z) = \\
&2^5\pi^{\frac{9}{2}} \sum_{j_1,j_2,j_3,j_4=0}^{\infty} \frac{(-1)^{j_1+j_2+j_3+j_4} z^{2+j_1+j_2+j_3+j_4}}{b\sqrt{2+j_1+j_2+j_3+j_4}} \int_{-1}^{1} \frac{b\,d\lambda}{a+b\lambda} \sin^{-1}\left(\frac{a+b\lambda}{\sqrt{AC}}\right),
\end{aligned} \tag{3.16}$$

which yields the expansion and defines $\hat{T}(z)$ for later use. As a practical matter, we still need to do the integral over λ. It can be evaluated in terms of dilogarithms of complex argument {Gröbner and Hofreiter [21], (341.4b)} which does not improve the situation much over direct evaluation. The substitution which we will make in the next section in order to convert to a series in ζ is numerically ill-conditioned so we need a method which will yield highly accurate values. The integral we need to evaluate is of the form

$$\int_0^v \frac{d\nu}{\nu}\sin^{-1}(\nu) = \sum_{k=0}^{\infty}\frac{(\frac{1}{2})_k v^{2k+1}}{k!(2k+1)^2}, \tag{3.17}$$

where we use the notation,

$$(g)_0 = 1, \quad (g)_k = g\cdot(g+1)\cdots(g+k-1), \quad k \geq 1. \tag{3.18}$$

The radius of convergence of the series (3.17) is $|v| = 1$. Its use when $v \approx \pm 1$ is too slow to be practical. We know that the nature of those singularities is $\sqrt{1-v^2}$. A uniformizing transformation which regularizes $\sqrt{1-v^2}$ will make the whole function regular at $v = \pm 1$. We choose the transformation,

$$v^2 = \frac{8w^2(3-w^2)}{9+6w^2+w^4}, \tag{3.19}$$

which converts,

$$\sqrt{(1-v^2)} = \frac{1-w^2}{1+\frac{1}{3}w^2}. \tag{3.20}$$

and makes the points $v = \pm 1$ into regular points $w = \pm 1$. There will be singular points at $w = \pm i\sqrt{3}$ which leaves a radius of convergence of 3 in w^2. This improvement is adequate for our purposes. The substitution of (3.19) in the series (3.17) must be done with care as many decimal places will be lost in the tripling of the radius of convergence. Never-the-less, we have carried this computation out in multiple precision arithmetic (58 decimals) and obtained adequate accuracy to evaluate the series coefficients in (3.16).

The contribution to the pressure p_{E2b} contains the integral,

$$\int \frac{d\vec{k}_1\, d\vec{k}_2\, d\vec{k}_3}{(\vec{k}_2-\vec{k}_1)^2(\vec{k}_1-\vec{k}_3)^2}\frac{\operatorname{sech}^2\left(\frac{1}{2}\mathrm{k}_1^2 - \frac{\mu}{2\mathrm{kT}}\right)}{\left[1+\exp\left(k_2^2-\frac{\mu}{kT}\right)\right]\left[1+\exp\left(k_3^2-\frac{\mu}{kT}\right)\right]}. \tag{3.21}$$

Let us make the change of variables $\vec{p}_1 = \vec{k}_2 - \vec{k}_1$ and $\vec{p}_2 = \vec{k}_3 - \vec{k}_1$. If we now expand (3.21) in powers of z, as we did above, we obtain,

$$4 \sum_{j_1,j_2,j_3=1}^{\infty} j_3(-1)^{j_1+j_2+j_3-3} z^{(j_1+j_2+j_3)\eta} \int \frac{d\vec{p}_1\, d\vec{p}_2}{p_1^2 p_2^2} d\vec{k}_1 \, \exp(-j_1 p_1^2 - j_2 p_2^2$$
$$-(j_1+j_2+j_3)k_1^2 - 2j_1\vec{p}_1\cdot\vec{k}_1 - 2j_2\vec{p}_2\cdot\vec{k}_1). \tag{3.22}$$

If we integrate over $\vec{k}_1$ by completing the square in Cartesian coordinates, then (3.22) becomes,

$$4\pi^{\frac{3}{2}} \sum_{j_1,j_2,j_3=1}^{\infty} \frac{j_3(-1)^{j_1+j_2+j_3-3} z^{(j_1+j_2+j_3)\eta}}{(j_1+j_2+j_3)^{\frac{3}{2}}} \int \frac{d\vec{p}_1\, d\vec{p}_2}{p_1^2 p_2^2}$$
$$\times \exp\left(\frac{-j_1(j_2+j_3)p_1^2 - j_2(j_1+j_3)p_2^2 + 2j_1 j_2 \vec{p}_1\cdot\vec{p}_2}{j_1+j_2+j_3}\right). \tag{3.23}$$

If we integrate over all the angles except that between $\vec{p}_1$ and $\vec{p}_2$ and denote the cosine of that angle by τ, then if we integrate over the magnitudes in the standard way for a quadratic form in the exponent, we get

$$8\pi^3\pi^{\frac{3}{2}} \sum_{j_1,j_2,j_3=1}^{\infty} \frac{j_3(-1)^{j_1+j_2+j_3-3} z^{(j_1+j_2+j_3)\eta}}{j_1 j_2 (j_1+j_2+j_3)^{\frac{1}{2}}}$$
$$\times \int_{-1}^{1} \frac{\sqrt{j_1 j_2}\, d\tau}{(j_3(j_2+j_1) + j_3^2 + j_1 j_2(1-\tau^2))^{\frac{1}{2}}}. \tag{3.24}$$

The final integral can now be evaluated to yield,

$$16\pi^{\frac{9}{2}} \sum_{j_1,j_2,j_3=1}^{\infty} \frac{j_3(-1)^{j_1+j_2+j_3-3} z^{(j_1+j_2+j_3)\eta}}{j_1 j_2 (j_1+j_2+j_3)^{\frac{1}{2}}} \sin^{-1}\left(\sqrt{\frac{j_1 j_2}{(j_1+j_3)(j_2+j_3)}}\right), \tag{3.25}$$

which can be rearranged in the slightly more convenient form,

$$16\pi^{\frac{9}{2}}\hat{\Theta}(z) = \tag{3.26}$$
$$16\pi^{\frac{9}{2}} \sum_{J=3}^{\infty} \frac{-(-z)^J}{\sqrt{J}} \sum_{j_1=1}^{J-2} \sum_{j_2=1}^{J-j_1-1} \frac{J-j_1-j_2}{j_1 j_2} \sin^{-1}\left(\sqrt{\frac{j_1 j_2}{(J-j_1)(J-j_2)}}\right),$$

which also defines $\hat{\Theta}(z)$ for later use.

Next we consider the e^4 corrections to the Debye-Hückel term. In the previous section we derived the series expansion for Ξ_{ion} in z_{ion}. It has only a linear term. We now consider the series expansion for Ξ in powers of $z = \exp[\mu/(kT)]$. To this end notice that

$$n(\vec{k}) = \sum_{n=1}^{\infty} (-1)^{n+1} z^n \exp[-n\epsilon(\vec{k})/(kT)]. \tag{3.27}$$

If we substitute this expansion in (2.30) and exchange the orders of summation and integration, we get,

$$\Xi(\vec{q},\omega_3) = \frac{2}{kT}\left(\frac{2mkT}{h^2}\right)^{\frac{3}{2}} \tag{3.28}$$

$$\times \sum_{n=1}^{\infty} (-1)^{n+1} z^n \Re \left\{ i \int_0^{\infty} dt \int d\vec{\kappa} \exp\left[-n\kappa^2 - t\left(\frac{\omega_3}{kT} + 2i\kappa\cdot\nu - i\nu^2\right)\right]\right\},$$

where we choose,

$$\vec{k} = \left(\frac{2mkT}{\hbar^2}\right)^{\frac{1}{2}} \vec{\kappa}, \qquad z = \exp[\mu/(kT)]. \tag{3.29}$$

The integral over κ is again of Gaussian form, so we can evaluate it as,

$$\Xi(\vec{q},\omega_3) = \frac{2}{kT}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \sum_{n=1}^{\infty} \frac{(-z)^n}{n^{\frac{3}{2}}} \int_0^{\infty} dt \exp\left(-\frac{\nu^2 t^2}{n} - \frac{\omega_3}{kT} t\right) \sin(t\nu^2). \tag{3.30}$$

The next step is to substitute (2.32) and (3.30) in (2.28), sum over ω_3 and then integrate over $\vec{q}$. It is evident from (2.28) that there are three types of terms, *i.e.*, electron-electron, electron-ion, and ion-ion. We will first treat the electron-electron terms. The counter term involves the limit as $|\vec{q}| \to 0$ of $\Xi(\vec{q},0)$, which by (3.30) and 3.896 (3) of Gradshteyn and Ryzhik [22] is,

$$\begin{aligned} \lim_{|\vec{q}|\to 0} \Xi(\vec{q},0) &= \lim_{|\vec{q}|\to 0} \frac{2}{kT}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \sum_{n=1}^{\infty} \frac{(-z)^n}{n^{\frac{3}{2}}} \left[\frac{n}{2}\,{}_1F_1\left(1;\frac{3}{2};-\frac{n}{4}\nu^2\right)\right] \\ &= \frac{2}{kT}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \sum_{n=1}^{\infty} \frac{(-z)^n}{n^{\frac{3}{2}}} \left(\frac{n}{2}\right), \end{aligned} \tag{3.31}$$

where ${}_1F_1(a;b;z)$ is the confluent hypergeometric function. With this result we get for the contribution from the $\omega_3 = 0$ terms,

$$\frac{8e^4}{kT}\left(\frac{2\pi mkT}{h^2}\right)^3\left(\frac{\hbar^2}{2mkT}\right)^{\frac{1}{2}}\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\frac{(-z)^{n_1+n_2}}{(n_1n_2)^{\frac{1}{2}}} \tag{3.32}$$
$$\times\int_0^{\infty}\frac{d\nu}{\nu^2}\left[{}_1F_1\left(1;\frac{3}{2};-\frac{n_1}{4}\nu^2\right)\,{}_1F_1\left(1;\frac{3}{2};-\frac{n_2}{4}\nu^2\right)-1\right].$$

We define and then note that,

$$\mathrm{erfi}(z)\equiv\frac{2}{\sqrt{\pi}}\int_0^z e^{x^2}\,dx=\frac{2z}{\sqrt{\pi}}\,\mathrm{e}^{z^2}\;{}_1F_1\left(1;\frac{3}{2};-z^2\right)=\frac{2z}{\sqrt{\pi}}\,{}_1F_1\left(\frac{1}{2};\frac{3}{2};z^2\right), \tag{3.33}$$

where $\mathrm{erfi}(z)$ is $-i\,\mathrm{erf}(iz)$ and erf is the standard error function. Thus we may re-express the integral in (3.32) as,

$$H(n_1,n_2) \tag{3.34}$$
$$=\int_0^{\infty}\frac{d\nu}{\nu^2}\left[\frac{\pi}{\sqrt{n_1n_2}\nu^2}\exp\left(-\frac{1}{4}(n_1+n_2)\nu^2\right)\mathrm{erfi}\left(\frac{\sqrt{n_1}}{2}\nu\right)\mathrm{erfi}\left(\frac{\sqrt{n_2}}{2}\nu\right)-1\right]$$

By means of an integration by parts, adding and subtracting the same term, and using (3.33), and using the known behavior of Dawson's integral [23], we can deduce that

$$H(n_1,n_2)=\frac{1}{3}\int_0^{\infty}\frac{d\nu}{\nu^2}\left[\sqrt{\frac{\pi}{n_2}}\frac{1}{\nu}\,\mathrm{erfi}\left(\frac{\sqrt{n_2}}{2}\nu\right)\exp\left(-\frac{n_2}{4}\nu^2\right)\right.$$
$$\left.+\sqrt{\frac{\pi}{n_1}}\frac{1}{\nu}\,\mathrm{erfi}\left(\frac{\sqrt{n_1}}{2}\nu\right)\exp\left(-\frac{n_1}{4}\nu^2\right)-2\right] \tag{3.35}$$
$$-\frac{n_1+n_2}{6}\int_0^{\infty}d\nu\left[\frac{\pi}{\sqrt{n_1n_2}\nu^2}\exp\left(-\frac{1}{4}(n_1+n_2)\nu^2\right)\mathrm{erfi}\left(\frac{\sqrt{n_1}}{2}\nu\right)\mathrm{erfi}\left(\frac{\sqrt{n_2}}{2}\nu\right)\right]$$

By performing yet another integration by parts, we may further deduce that,

$$H(n_1,n_2)=-\frac{\sqrt{\pi}}{12}\int\frac{d\nu}{\nu}\left[\left(\sqrt{n_2}+\frac{2(n_1+n_2)}{\sqrt{n_2}}\right)\mathrm{erfi}\left(\frac{\sqrt{n_2}}{2}\nu\right)\exp\left(-\frac{n_2}{4}\nu^2\right)\right.$$
$$\left.+\left(\sqrt{n_1}+\frac{2(n_1+n_2)}{\sqrt{n_1}}\right)\mathrm{erfi}\left(\frac{\sqrt{n_1}}{2}\nu\right)\exp\left(-\frac{n_1}{4}\nu^2\right)\right] \tag{3.36}$$
$$+\frac{(n_1+n_2)^2\pi}{12\sqrt{n_1n_2}}\int_0^{\infty}d\nu\exp\left(-\frac{1}{4}(n_1+n_2)\nu^2\right)\mathrm{erfi}\left(\frac{\sqrt{n_1}}{2}\nu\right)\mathrm{erfi}\left(\frac{\sqrt{n_2}}{2}\nu\right)$$

These integrals can be done. First we need,

$$I_1 = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{d\nu}{\nu} \exp(-\nu^2) \int_0^\nu \exp(\xi^2)\, d\xi, \tag{3.37}$$

where we have re-expressed erfi by (3.33). Gradshteyn and Ryzhik [22] give the result (6.317, as revised in the latest edition),

$$\frac{2}{\sqrt{\pi}} \int_0^\infty dx\, \exp(-a^2x^2)\sin(bx) \int_0^{ax} dt\, \exp(t^2) = \frac{\sqrt{\pi}}{2a} \exp\left(-\frac{b^2}{4a^2}\right) \tag{3.38}$$

If we multiply both sides of this equation by $\exp(-pb)\, db$ and integrate from $b = 0$ to $b = \infty$ then by Gradshteyn and Ryzhik [22] 3.893(1) we get in the limit as $p \to 0$,

$$I_1 = \frac{\pi}{2}. \tag{3.39}$$

The other integral that we need is given by the last line in (3.36). It may be re-expressed by (3.33) as

$$\begin{aligned} I_2 = {} & \frac{\sqrt{n_1 n_2}}{\pi} \\ & \times \int_0^\infty \nu^2 d\nu\, \exp\left(-\frac{1}{4}(n_1+n_2)\nu^2\right) {}_1F_1\left(\frac{1}{2};\frac{3}{2};\frac{n_1}{4}\nu^2\right) {}_1F_1\left(\frac{1}{2};\frac{3}{2};\frac{n_2}{4}\nu^2\right), \end{aligned} \tag{3.40}$$

where the ${}_1F_1$'s are confluent hypergeometric functions. By a change of variables we can cast (3.40) into the form of Gradshteyn and Ryzhik [22] 7.622(1), so that we get

$$I_2 = \frac{2}{\sqrt{\pi}} \frac{1}{\sqrt{n_1+n_2}} F\left(\frac{1}{2},\frac{1}{2};\frac{3}{2};1\right) = \sqrt{\frac{\pi}{n_1+n_2}}, \tag{3.41}$$

where F is a hypergeometric function. Thus we obtain,

$$\begin{aligned} H(n_1,n_2) = {} & -\frac{\pi^{\frac{3}{2}}}{24} \\ & \times \left\{ \sqrt{n_1} + \sqrt{n_2} + 2(n_1+n_2)\left[\frac{1}{\sqrt{n_1}} + \frac{1}{\sqrt{n_2}} - \left(\frac{1}{n_1}+\frac{1}{n_2}\right)^{1/2}\right]\right\} \end{aligned} \tag{3.42}$$

Thus the coefficients in (3.32) have been explicitly evaluated to give, ($\omega_3 = 0$)

$$p_{DH4,c1} \equiv \frac{8e^4}{kT}\left(\frac{2\pi mkT}{h^2}\right)^3\left(\frac{\hbar^2}{2mkT}\right)^{\frac{1}{2}}\hat{\psi}(z),$$
$$\hat{\psi}(z) = \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\frac{(-z)^{n_1+n_2}}{(n_1n_2)^{\frac{1}{2}}}H(n_1,n_2). \tag{3.43}$$

We take note that when n_2 is finite and n_1 is very large that $H(n_1, n_2)$ is proportional to $\sqrt{n_1}$ so the series in (3.43) converges geometrically for small enough z.

For the terms with $\omega_3 \neq 0$ we get,

$$\frac{256\pi^3e^4}{(2\pi)^3kT}\left(\frac{2\pi mkT}{h^2}\right)^3\left(\frac{\hbar^2}{2mkT}\right)^{\frac{1}{2}}\sum_{\omega_3\neq 0}\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\frac{(-z)^{n_1+n_2}}{(n_1n_2)^{\frac{3}{2}}}\int_0^{\infty}\frac{d\nu}{\nu^2}\int_0^{\infty}dt_1\int_0^{\infty}dt_2$$
$$\times\left\{\exp\left[-\nu^2\left(\frac{t_1^2}{n_1}+\frac{t_2^2}{n_2}\right)-\frac{|\omega_3|}{kT}(t_1+t_2)\right]\sin(t_1\nu^2)\sin(t_2\nu^2)\right\}. \tag{3.44}$$

Performing the sum over ω_3, we obtain,

$$\frac{32e^4}{kT}\left(\frac{2\pi mkT}{h^2}\right)^3\left(\frac{\hbar^2}{2mkT}\right)^{\frac{1}{2}}\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\frac{(-z)^{n_1+n_2}}{(n_1n_2)^{\frac{3}{2}}}$$
$$\times\int_0^{\infty}\frac{d\nu}{\nu^2}\int_0^{\infty}dt_1\int_0^{\infty}dt_2\left\{\exp\left[-\nu^2\left(\frac{t_1^2}{n_1}+\frac{t_2^2}{n_2}\right)\right]\frac{2\sin(t_1\nu^2)\sin(t_2\nu^2)}{\exp[2\pi(t_1+t_2)]-1}\right\}. \tag{3.45}$$

Using the identity, $2\sin(t_1\nu^2)\sin(t_2\nu^2) = \cos[\nu^2(t_1-t_2)]-\cos[\nu^2(t_1+t_2)]$, and a known integral [Gradshteyn and Ryzhik [22] 3.945 (2)], we may evaluate the integral over ν. The result is,

$$-\frac{16e^4}{kT}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{5}{2}}\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\frac{(-z)^{n_1+n_2}}{(n_1n_2)^{\frac{3}{2}}}\int_0^{\infty}dt_1\int_0^{\infty}dt_2\left\{\exp[2\pi(t_1+t_2)]-1\right\}^{-1}$$
$$\times\left\{\left[\left(\frac{t_1^2}{n_1}+\frac{t_2^2}{n_2}\right)^2+(t_1-t_2)^2\right]^{\frac{1}{4}}\cos\left[\frac{1}{2}\arctan\left(\frac{t_1-t_2}{\frac{t_1^2}{n_1}+\frac{t_2^2}{n_2}}\right)\right]\right.$$
$$\left.-\left[\left(\frac{t_1^2}{n_1}+\frac{t_2^2}{n_2}\right)^2+(t_1+t_2)^2\right]^{\frac{1}{4}}\cos\left[\frac{1}{2}\arctan\left(\frac{t_1+t_2}{\frac{t_1^2}{n_1}+\frac{t_2^2}{n_2}}\right)\right]\right\}. \tag{3.46}$$

By means of the trigonometric identity,

$$\cos\left[\frac{1}{2}\arctan\left(\frac{a}{b}\right)\right] = \sqrt{\frac{1}{2}\left(1+\frac{b}{\sqrt{a^2+b^2}}\right)}, \tag{3.47}$$

we may rewrite (3.46) in a simpler form as,

$$
\begin{aligned}
p_{DH4,c2} &= -\frac{8\sqrt{2}e^4}{kT}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{5}{2}} \hat{W}(z) \\
\hat{W}(z) &= \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\frac{(-z)^{n_1+n_2}}{(n_1 n_2)^{\frac{3}{2}}}\int_0^{\infty} dt_1 \int_0^{\infty} dt_2 \left\{\exp[2\pi(t_1+t_2)]-1\right\}^{-1} \\
&\times \left\{\sqrt{\left[\left(\frac{t_1^2}{n_1}+\frac{t_2^2}{n_2}\right)^2+(t_1-t_2)^2\right]^{\frac{1}{2}}+\frac{t_1^2}{n_1}+\frac{t_2^2}{n_2}}\right. \\
&\left. -\sqrt{\left[\left(\frac{t_1^2}{n_1}+\frac{t_2^2}{n_2}\right)^2+(t_1+t_2)^2\right]^{\frac{1}{2}}+\frac{t_1^2}{n_1}+\frac{t_2^2}{n_2}}\right\}. \qquad (3.48)
\end{aligned}
$$

These integrals are evaluated numerically using the Romberg integration method (Numerical Recipes [24], recoded in double and multiple precision for the case of a double integral). First however, we make the change of variables,

$$
t_1 = (\eta^2+\xi^2)/\sqrt{2}, \quad t_2 = (\eta^2-\xi^2)/\sqrt{2}. \qquad (3.49)
$$

to insure that the integrand is analytic at the origin.

Next we compute the results for the ion-ion case. First, in line with equation (3.31) above, we can compute from (2.32) that

$$
\begin{aligned}
\lim_{|\vec{q}|\to 0}\Xi_{\mathrm{ion}}(\vec{q},0) &= -\lim_{|\vec{q}|\to 0}\frac{z_{\mathrm{ion}}}{kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}}\left[\frac{1}{2}\,{}_1F_1\left(1;\frac{3}{2};-\frac{\nu^2}{4}\right)\right] \\
&= -\frac{z_{\mathrm{ion}}}{2kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}}. \qquad (3.50)
\end{aligned}
$$

Thus, using (2.28), we find that the ion-ion contribution for $\omega_3 = 0$ is

$$
\frac{Z^4 e^4 z_{\mathrm{ion}}^2}{\sqrt{\pi}kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{5}{2}}\int_0^{\infty}\frac{d\nu}{\nu^2}\left\{\left[{}_1F_1\left(1;\frac{3}{2};-\frac{\nu^2}{4}\right)\right]^2-1\right\}. \qquad (3.51)
$$

This integral is the special case $n_1 = n_2 = 1$ of the integral in (3.32). Thus, from the value of $H(1,1)$ of (3.42), we get for (3.51),

$$p_{DH,c3} = -\frac{\pi Z^4 e^4 z_{\text{ion}}^2}{12kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{5}{2}}\left(5-2\sqrt{2}\right). \tag{3.52}$$

For the $\omega_3 \neq 0$, ion-ion contribution we get

$$\begin{aligned}&\frac{4e^4 Z^4 z_{\text{ion}}^2}{\sqrt{\pi}kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{5}{2}}\int_0^\infty dt_1\int_0^\infty dt_2\int_0^\infty \frac{d\nu}{\nu^2}\\ &\times\left\{\frac{\exp[-(t_1^2+t_2^2)\nu^2]2\sin(\nu^2 t_1)\sin(\nu^2 t_2)}{\exp[2\pi(t_1+t_2)]-1}\right\}.\end{aligned} \tag{3.53}$$

As in (3.46), the integral over $d\nu$ can be evaluated, giving the result

$$\begin{aligned}p_{DH,c4} = -\frac{2\sqrt{2}e^4 Z^4 z_{\text{ion}}^2}{kT}&\left(\frac{2\pi MkT}{h^2}\right)^{\frac{5}{2}}\int_0^\infty dt_1\int_0^\infty dt_2\left\{\exp[2\pi(t_1+t_2)]-1\right\}^{-1}\\ &\times\left\{\sqrt{[(t_1^2+t_2^2)^2+(t_1-t_2)^2]^{\frac{1}{2}}+t_1^2+t_2^2}\right.\\ &\left.-\sqrt{[(t_1^2+t_2^2)^2+(t_1+t_2)^2]^{\frac{1}{2}}+t_1^2+t_2^2}\right\}.\end{aligned} \tag{3.54}$$

Finally we compute the results for the electron-ion case. The terms for $\omega_3 \neq 0$ are,

$$\begin{aligned}&-\frac{16Z^2e^4 z_{\text{ion}}}{\sqrt{\pi}kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{5}{2}}\left(\frac{m}{M}\right)\sum_{\omega_3\neq 0}\sum_{n=1}^\infty\frac{(-z)^n}{n^{\frac{3}{2}}}\int_0^\infty\frac{d\nu}{\nu^2}\int_0^\infty dt_1\int_0^\infty dt_2\\ &\times\exp\left[-\left(\frac{m}{M}t_1^2+\frac{1}{n}t_2^2\right)\nu^2-\frac{|\omega_3|}{kT}(t_1+t_2)\right]\sin\left(\frac{m}{M}t_1\nu^2\right)\sin(t_2\nu^2).\end{aligned} \tag{3.55}$$

Doing the sum over ω_3, we get,

$$\begin{aligned}&-\frac{16Z^2e^4 z_{\text{ion}}}{\sqrt{\pi}kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{5}{2}}\left(\frac{m}{M}\right)\sum_{n=1}^\infty\frac{(-z)^n}{n^{\frac{3}{2}}}\int_0^\infty\frac{d\nu}{\nu^2}\int_0^\infty dt_1\int_0^\infty dt_2\\ &\times\exp\left[-\left(\frac{m}{M}t_1^2+\frac{1}{n}t_2^2\right)\nu^2\right]\frac{2\sin\left(\frac{m}{M}t_1\nu^2\right)\sin(t_2\nu^2)}{\exp[2\pi(t_1+t_2)]-1}.\end{aligned} \tag{3.56}$$

Again the integral over ν can be evaluated, and it gives,

$$
\begin{aligned}
p_{DH,c6} = {} & \frac{8\sqrt{2}Z^2e^4z_{\text{ion}}}{kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{5}{2}}\left(\frac{m}{M}\right) \\
& \times \sum_{n=1}^{\infty}\frac{(-z)^n}{n^{\frac{3}{2}}}\int_0^{\infty}dt_1\int_0^{\infty}dt_2\{\exp[2\pi(t_1+t_2)]-1\}^{-1} \\
& \times\left\{\sqrt{\left[\left(\frac{m}{M}t_1^2+\frac{1}{n}t_2^2\right)^2+\left(\frac{m}{M}t_1-t_2\right)^2\right]^{\frac{1}{2}}+\frac{m}{M}t_1^2+\frac{1}{n}t_2^2}\right. \\
& \left.-\sqrt{\left[\left(\frac{m}{M}t_1^2+\frac{1}{n}t_2^2\right)^2+\left(\frac{m}{M}t_1+t_2\right)^2\right]^{\frac{1}{2}}+\frac{m}{M}t_1^2+\frac{1}{n}t_2^2}\right\}. \qquad (3.57)
\end{aligned}
$$

The electron-ion terms for the case of $\omega_3 = 0$ are,

$$
\begin{aligned}
p_{DH,c5} = {} & -\frac{4Z^2e^4z_{\text{ion}}}{\sqrt{\pi}kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{5}{2}}\left(\frac{m}{M}\right)\sum_{n=1}^{\infty}\frac{(-z)^n}{n^{\frac{1}{2}}}\int_0^{\infty}\frac{d\nu}{\nu^2} \qquad (3.58) \\
& \times\left[{}_1F_1\left(1;\frac{3}{2};-\frac{m}{4M}\nu^2\right)\,{}_1F_1\left(1;\frac{3}{2};-\frac{n}{4}\nu^2\right)-1\right].
\end{aligned}
$$

Since, normally the mass of the ion is much larger than the mass of the electron, it is worthwhile to examine the behavior near the the limit as $\frac{m}{M}\to 0$. In the case of the $\omega_3\neq 0$ terms, (3.57), the terms in the integrand cancel in this limit. The first order expansion in $\frac{m}{M}$ yields a convergent integral. Thus the result here is of the order of $\frac{m}{M}$ and so can normally be neglected. However, even though the coefficients in the z series in (3.57) are each of order $\frac{m}{M}$ in the small $\frac{m}{M}$ limit, when we interchange the order of sizes and let $\zeta^{\frac{2}{3}}\frac{m}{M}\to\infty$ then the limit is of the order of ζ with the coefficient independent of $\frac{m}{M}$. For very large values of ζ, this term should also be included. For the $\omega_3 = 0$ terms, (3.58), by the asymptotic behavior of Dawson's integral [23], we can easily see that ${}_1F_1(1;\frac{3}{2};-\frac{n}{4}\nu^2)\propto\nu^{-1}$ for large ν. Thus ${}_1F_1(1;\frac{3}{2};-\frac{m}{4M}\nu^2)\approx 1$ where its contribution is significant. Hence we can scale out the behavior on n by choosing $\tilde{\nu}=\sqrt{\frac{n}{4}}\nu$. Therefore, the contribution from the ion-electron terms is approximately,

$$
p_{DH,c5}\approx\frac{2Z^2e^4z_{\text{ion}}}{\sqrt{\pi}kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{5}{2}}\left(\frac{m}{M}\right)\left(\frac{z}{1+z}\right)\int_0^{\infty}\frac{d\tilde{\nu}}{\tilde{\nu}^2}\left[{}_1F_1\left(1;\frac{3}{2};-\tilde{\nu}^2\right)-1\right]
$$

$$= -\frac{\pi Z^2 e^4 z_{\rm ion}}{2kT}\left(\frac{2\pi MkT}{h^2}\right)^{\frac{5}{2}}\left(\frac{m}{M}\right)\left(\frac{z}{1+z}\right). \qquad (3.59)$$

where the integral was done by an integration by parts and the use of Gradshteyn and Ryzhik [22] 7.612(1).

In summary, to obtain the actual numerical values of the fugacity expansions, we need to evaluate, (i) for the ion-ion case, the double integral in (3.54), (ii) for the electron-ion case, we have evaluated all the necessary integrals, and for (iii) the electron-electron case, we need the double integrals in (3.48), where $n_1 + n_2 \leq \mathcal{N}$, with $\mathcal{N}$ the highest order sought in the series. Notice that the ion-ion integral is the special case $n_1 = n_2 = 1$ of the corresponding electron-electron integral.

4 SOLUTION OF THE FUGACITY EQUATIONS

In this section we need to eliminate the fugacities z and $z_{\rm ion}$ and re-express the thermodynamic quantities in terms of observable variables. From standard quantum statistical mechanics, the required functions may be obtained from the grand partition function $\mathcal{Q}$ by means of

$$\frac{p\Omega}{kT} = \log \mathcal{Q}(\Omega, T, z, z_{\rm ion}), \qquad (4.1)$$

$$ZN = z\frac{\partial}{\partial z}\log \mathcal{Q}(\Omega, T, z, z_{\rm ion})\Big|_{\Omega, T, z_{\rm ion}}, \qquad (4.2)$$

$$N_{\rm ion} = z_{\rm ion}\frac{\partial}{\partial z_{\rm ion}}\log \mathcal{Q}(\Omega, T, z, z_{\rm ion})\Big|_{\Omega, T, z}, \qquad (4.3)$$

where $N_{\rm ion} = N$ for system neutrality. Gathering together our results from other sections we have,

$$\log \mathcal{Q}(\Omega, T, z, z_{\rm ion}) = z_{\rm ion}\Omega\left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}} + 2\Omega\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\Bigg\{\frac{I_{\frac{3}{2}}(z)}{\Gamma(\frac{5}{2})}$$
$$+\frac{1}{\pi}\left(\frac{2\pi me^4}{h^2kT}\right)^{\frac{1}{2}}\hat{X}(z) + \frac{\sqrt{\pi}}{3}\left(\frac{2\pi me^4}{h^2kT}\right)^{\frac{3}{4}}\left[Z^2\left(\frac{M}{m}\right)^{\frac{3}{2}} z_{\rm ion} + \frac{2}{\sqrt{\pi}}I_{-\frac{1}{2}}(z)\right]^{\frac{3}{2}}$$
$$-\left(\frac{2\pi me^4}{h^2kT}\right)\left[\frac{1}{2}\hat{T}(z) - \hat{\Theta}(z) + \frac{2}{\sqrt{\pi}}\hat{\psi}(z) - 4\sqrt{2}\hat{W}(z) - \frac{\pi}{4}Z^2\left(\frac{M}{m}\right)^{\frac{3}{2}}\frac{z_{\rm ion}z}{1+z}\right.$$

$$+(0.2842582246-0.006578041016)Z^4\left(\frac{M}{m}\right)^{\frac{5}{2}} z_{\text{ion}}^2\Bigg] + o(e^4)\Bigg\} \tag{4.4}$$

where h is Planck's constant and the numerical coefficients in the last line will be explained in the next section [See, (5.22)]. The quantities I_n, $\hat{X}$, $\hat{T}$, $\hat{\Theta}$, $\hat{\psi}$, and $\hat{W}$ are given by equations (3.5), (3.7), (3.16), (3.26), (3.43), (3.46), and (3.48). Explicit numerical representations for these quantities are given in the next section. The following notation will be useful,

$$\zeta = \frac{ZN}{2\Omega}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}, \quad \epsilon = \left(\frac{2\pi me^4}{h^2kT}\right)^{\frac{1}{4}}, \quad r_b = \left[\frac{3\Omega}{4\pi N}\right]^{\frac{1}{3}}, \quad x_0 = \frac{r_b}{a_0},$$
$$y^2 = \frac{Ze^2}{r_bkT} = 2\left(\frac{Z}{9\pi}\right)^{\frac{1}{3}}\zeta^{\frac{2}{3}}x_0, \quad \epsilon = \left(\frac{3}{8\pi Z^2\zeta}\right)^{\frac{1}{6}} y = \left(\frac{\zeta}{3\pi^2 Z}\right)^{\frac{1}{6}}\sqrt{x_0}, \tag{4.5}$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius. We have previously defined ζ, y and r_b [(2.16) and (3.1)], but include them here for convenience. Equations (4.2) and (4.3) become,

$$ZN = 2\Omega\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\Bigg\{\frac{I_{\frac{1}{2}}(z)}{\Gamma(\frac{3}{2})} + \frac{1}{\pi}\epsilon^2\left[I_{-\frac{1}{2}}(z)\right]^2$$
$$+\epsilon^3\left[Z^2\left(\frac{M}{m}\right)^{\frac{3}{2}} z_{\text{ion}} + \frac{2}{\sqrt{\pi}}I_{-\frac{1}{2}}(z)\right]^{\frac{1}{2}} z\frac{d}{dz}I_{-\frac{1}{2}}(z)$$
$$-\epsilon^4\Bigg[\frac{1}{2}z\frac{d}{dz}\hat{T}(z) - z\frac{d}{dz}\hat{\Theta}(z) + \frac{2}{\sqrt{\pi}}z\frac{d}{dz}\hat{\psi}(z) - 4\sqrt{2}z\frac{d}{dz}\hat{W}(z)$$
$$-\frac{\pi}{4}Z^2\left(\frac{M}{m}\right)^{\frac{3}{2}}\frac{z_{\text{ion}}z}{(1+z)^2}\Bigg] + o(e^4)\Bigg\} \tag{4.6}$$

$$N_{\text{ion}} = z_{\text{ion}}\Omega\left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}}$$
$$\times\Bigg\{1 + \sqrt{\pi}\epsilon^3Z^2\left[Z^2\left(\frac{M}{m}\right)^{\frac{3}{2}} z_{\text{ion}} + \frac{2}{\sqrt{\pi}}I_{-\frac{1}{2}}(z)\right]^{\frac{1}{2}}$$
$$+\epsilon^4\left[\frac{\pi}{2}Z^2\frac{z}{(1+z)} - 4(0.2776801836)Z^4\left(\frac{M}{m}\right)z_{\text{ion}}\right] + o(e^4)\Bigg\}, \tag{4.7}$$

where $z\frac{d}{dz}\hat{X}(z) = [I_{-\frac{1}{2}}(z)]^2$ has been used. These equations are two, coupled, non-linear equations in the two unknowns, z and z_{ion}. Fortunately, they can be solved through order ϵ^4 in a fairly straightforward manner. First, given z, equation (4.7) yields,

$$z_{\text{ion}} = \frac{2\zeta}{Z}\left(\frac{m}{M}\right)^{\frac{3}{2}}\left\{1-\sqrt{\pi}Z^2\epsilon^3\left[2Z\zeta+\frac{2}{\sqrt{\pi}}I_{-\frac{1}{2}}(z)\right]^{\frac{1}{2}}\right.$$

$$\left.-\epsilon^4\left[\frac{\pi}{2}Z^2\frac{z}{(1+z)}-8(0.2776801836)Z^3\left(\frac{m}{M}\right)^{\frac{1}{2}}\zeta\right]+o(e^4)\right\}, \tag{4.8}$$

where the leading order of z in powers of ϵ is sufficient to the accuracy required here.

As the derivatives of the various functions of the fugacity are more natural in terms of $d\log z$, it is most convenient to solve (4.6) by means of the expansion

$$z(\zeta,\epsilon) = \exp\left(\eta_0(\zeta)+\eta_2(\zeta)\epsilon^2+\eta_3(\zeta)\epsilon^3+\eta_4(\zeta)\epsilon^4+\cdots\right),$$
$$z_0(\zeta) = \exp\left(\eta_0(\zeta)\right). \tag{4.9}$$

To leading order in ϵ, *i.e.*, ϵ^0, (4.6) yields

$$\zeta = \frac{I_{\frac{1}{2}}(z)}{\Gamma(\frac{3}{2})}. \tag{4.10}$$

Since, [5], the right-hand side is a series in z beginning with $z+\ldots$, the series may be reverted to give $z_0(\zeta)$ as its solution. The substitution of $z_0(\zeta)$ for z in (4.8) completes the expression of z_{ion} in terms of observable quantities to the order ϵ^4 and gives us $z_{\text{ion}}(\zeta)$. The reversion procedure has been done by Baker and Johnson [5] through order ζ^{35}. They carried at least 58 decimal places as the equations are rather ill conditioned. See also, [25]. The solutions for the remaining terms are

$$\eta_2(\zeta) = -\frac{1}{\sqrt{\pi}}I_{-\frac{1}{2}}(z_0(\zeta)), \tag{4.11}$$

$$\eta_3(\zeta) = -\sqrt{\pi}\left[Z^2\left(\frac{M}{m}\right)^{\frac{3}{2}}z_{\text{ion}}+\frac{2}{\sqrt{\pi}}I_{-\frac{1}{2}}(z_0(\zeta))\right]^{\frac{1}{2}}\frac{z\frac{d}{dz}I_{-\frac{1}{2}}(z_0(\zeta))}{I_{-\frac{1}{2}}(z_0(\zeta))}, \tag{4.12}$$

$$\eta_4(\zeta) = \frac{3}{2\pi}I_{-\frac{1}{2}}(z_0(\zeta))z\frac{d}{dz}I_{-\frac{1}{2}}(z_0(\zeta))$$
$$+\frac{\sqrt{\pi}}{I_{-\frac{1}{2}}(z_0(\zeta))}\left[\frac{1}{2}z\frac{d}{dz}\hat{T}(z_0(\zeta))-z\frac{d}{dz}\hat{\Theta}(z_0(\zeta))+\frac{2}{\sqrt{\pi}}z\frac{d}{dz}\hat{\psi}(z_0(\zeta))\right.$$
$$\left.-4\sqrt{2}z\frac{d}{dz}\hat{W}(z_0(\zeta))-\frac{\pi}{4}Z^2\left(\frac{M}{m}\right)^{\frac{3}{2}}\frac{z_{\text{ion}}(\zeta)z_0(\zeta)}{(1+z_0(\zeta))^2}\right], \tag{4.13}$$

where the leading order of $z_{\rm ion}(\zeta)$ in powers of ϵ is sufficient to the accuracy required here.

When these results are back substituted into (4.4) and expanded in powers of y, we get,

$$\frac{P\Omega}{NkT} = G_0(\zeta) + G_2(\zeta)y^2 + G_3(\zeta)y^3 + G_4(\zeta)y^4 + o(e^4). \tag{4.14}$$

The coefficients in this expansion are,

$$G_0(\zeta) = 1 + Z\frac{2I_{\frac{3}{2}}(z_0(\zeta))}{3I_{\frac{1}{2}}(z_0(\zeta))}, \tag{4.15}$$

$$G_2(\zeta) = -\left(\frac{3Z}{8\pi\zeta}\right)^{\frac{1}{3}}\left(\frac{1}{\sqrt{\pi}}I_{-\frac{1}{2}}(z_0(\zeta)) - \frac{1}{\pi\zeta}\hat{X}(z_0(\zeta))\right), \tag{4.16}$$

$$\begin{aligned} G_3(\zeta) = -\left(\frac{3}{8\zeta}\right)^{\frac{1}{2}}\Bigg\{&\left(\hat{Z} + \frac{z\frac{d}{dz}I_{-\frac{1}{2}}(z_0(\zeta))}{I_{-\frac{1}{2}}(z_0(\zeta))}\right)\left[2\hat{Z}\zeta + \frac{2}{\sqrt{\pi}}I_{-\frac{1}{2}}(z_0(\zeta))\right]^{\frac{1}{2}} \\ &-\frac{1}{3\zeta}\left[2\hat{Z}\zeta + \frac{2}{\sqrt{\pi}}I_{-\frac{1}{2}}(z_0(\zeta))\right]^{\frac{3}{2}}\Bigg\}, \end{aligned} \tag{4.17}$$

$$\begin{aligned} G_4(\zeta) = &\frac{1}{4\sqrt[3]{Z}}\left(\frac{3}{\pi\zeta}\right)^{\frac{2}{3}}\Bigg\{\frac{3}{2\pi}I_{-\frac{1}{2}}(z_0(\zeta))z\frac{d}{dz}I_{-\frac{1}{2}}(z_0(\zeta)) - \frac{1}{2\pi^{\frac{3}{2}}\zeta}\left(I_{-\frac{1}{2}}(z_0(\zeta))\right)^3 \\ &+\frac{\sqrt{\pi}}{I_{-\frac{1}{2}}(z_0(\zeta))}\Bigg[\frac{1}{2}z\frac{d}{dz}\hat{T}(z_0(\zeta)) - z\frac{d}{dz}\hat{\Theta}(z_0(\zeta)) + \frac{2}{\sqrt{\pi}}z\frac{d}{dz}\hat{\psi}(z_0(\zeta)) \\ &-4\sqrt{2}z\frac{d}{dz}\hat{W}(z_0(\zeta)) - \frac{\pi}{2}\hat{Z}\frac{\zeta z_0(\zeta)}{(1+z_0(\zeta))^2}\Bigg] - \frac{1}{\zeta}\Bigg[\frac{1}{2}\hat{T}(z_0(\zeta)) - \hat{\Theta}(z_0(\zeta)) \\ &+\frac{2}{\sqrt{\pi}}\hat{\psi}(z_0(\zeta)) - 4\sqrt{2}\hat{W}(z_0(\zeta)) - 4(0.2776801836)\hat{Z}^2\left(\frac{m}{M}\right)^{\frac{1}{2}}\zeta^2\Bigg]\Bigg\}, \end{aligned} \tag{4.18}$$

To repeat the remark after (4.4),the quantities y, ζ, I_n, $\hat{X}$, $\hat{T}$, $\hat{\Theta}$, $\hat{\psi}$, $z_0(\zeta)$, and $\hat{W}$ are given by equations (3.5), (3.7), (3.16), (3.26), (3.43), (3.46), (3.48), (4.5), and (4.9). Explicit numerical representations for these quantities and the necessary derivatives are given in the next section.

Baker and Johnson [8] report that for a pure element, $\hat{Z} = Z$, and in the case of mixtures,

$$Z = \frac{\sum_{\rm species} N_j Z_j}{\sum_{\rm species} N_j}, \quad \hat{Z} = \frac{\sum_{\rm species} N_j Z_j^2}{\sum_{\rm species} N_j Z_j}, \tag{4.19}$$

where N_j is the number of ions and Z_j is the nuclear charge in each species.

5 EVALUATION OF THE COEFFICIENTS OF THE PERTURBATION EXPANSION

In a previous section we have derived series expansions in the fugacity z for the various functions needed to calculate the expansion of the pressure in powers of the electronic charge. While is is possible to express the fugacity in terms of the de Broglie density (3.1) and the temperature by (4.9-4.13) and to give a compact representation thereof, it is usually more convenient to work directly in terms of the de Broglie density. It is our aim in this section to produce representations of the various quantities as functions of the de Broglie density which are accurate to within about 0.1%. The series for the fugacity in powers of the de Broglie density (for the ideal Fermi gas which is what we actually require) has been given by Baker and Johnson [5]. It can be substituted into the expressions of the previous sections to give the required series in the de Broglie density. Then following the method of Padé approximants [11], we can construct the require representations. First, we give [9] the following representation for the fugacity $z_0(\zeta)$ as,

$$z_0(\zeta) \approx \exp\{\zeta[\hat{\theta}(\zeta)]^{\frac{1}{3}}\} - 1, \tag{5.1}$$

where,

$$\hat{\theta}(\zeta) = \tag{5.2}$$
$$\frac{1 + 0.23728611\zeta + 2.4737617\times 10^{-2}\zeta^2 + 1.4222435\times 10^{-3}\zeta^3}{1 + 0.67662597\zeta + 0.14567696\zeta^2 + 1.4254337\times 10^{-2}\zeta^3 + 8.0482522\times 10^{-4}\zeta^4}$$

within 0.1%. This representation follows from the series expansion of (4.10) and the well-known asymptotic result [20]

$$\zeta \asymp \frac{(\log z)^{\frac{3}{2}}}{\Gamma(\frac{5}{2})}, \quad z \to \infty. \tag{5.3}$$

The symbol $\asymp$ means "is asymptotic to."

The general method we use to obtain these representations is first to compute a fair number of terms in the series expansion. Even with an explicit representation for the series as a function of the fugacity, care must be taken in the re-expression as a function of the de Broglie density because the problem is numerically ill-conditioned, and many decimal places can be lost. We have found that the retention of 58 decimals is sufficient for all our purposes. The next step is to determine the asymptotic behavior. From this information, we compute a function of the original series (*e.g.*, the cube) which can be exactly represented, both at the origin and at infinity, by a Padé approximant. We then compute a sequence of Padé approximants and use the lowest order one which gives the desired degree of accuracy. Since, for our problems, these sequences converge fairly quickly, this method seems to be quite efficient.

The most straightforward one follows immediately from (4.10)

$$I_{\frac{1}{2}}(\zeta) \equiv I_{\frac{1}{2}}(z_0(\zeta)) = \frac{\sqrt{\pi}\zeta}{2}. \tag{5.4}$$

Next, Baker and Johnson [5] have given the representation,

$$\begin{aligned} &\frac{2I_{\frac{3}{2}}(z_0(\zeta))}{3I_{\frac{1}{2}}(z_0(\zeta))} \equiv g_0(\zeta) \\ \approx &\left[\frac{1+0.61094880\zeta+0.12660436\zeta^2+0.0091177644\zeta^3}{1+0.080618739\zeta}\right]^{\frac{1}{3}}, \end{aligned} \tag{5.5}$$

This representation, and all the subsequent ones given in this section are accurate to about 0.1 %, unless otherwise noted. The next ingredient we need was given by Baker and Johnson [6],

$$I_{-\frac{1}{2}}(\zeta) \equiv I_{-\frac{1}{2}}(z_0(\zeta)) = \frac{\sqrt{\pi}\zeta}{g_0(\zeta)+\zeta g_0'(\zeta)} \approx \sqrt{\pi}\zeta\left[\frac{v_3(\zeta)}{u_5(\zeta)}\right]^{\frac{1}{3}}, \tag{5.6}$$

where

$$\begin{aligned} v_3(\zeta) &= 1+0.17549205\zeta+1.1833437\times10^{-2}\zeta^2+3.0923597\times10^{-4}\zeta^3, \\ u_5(\zeta) &= 1+1.2361522\zeta+0.54327035\zeta^2+9.7985998\times10^{-2}\zeta^3 \\ &\quad +6.1912639\times10^{-3}\zeta^4+1.6191557\times10^{-4}\zeta^5. \end{aligned} \tag{5.7}$$

For $\Theta(\zeta)$, using the result,

$$\Theta(\zeta) \asymp \frac{3}{2\pi}\zeta \quad \text{as} \quad \zeta\to\infty, \tag{5.8}$$

which is obtained by taking the limit as $z\to\infty$ of Θ and ζ and evaluating their integral definitions, Baker and Johnson [8] obtained the representation

$$\Theta(\zeta) \approx \frac{\mu_6(\zeta)}{\theta_5(\zeta)}, \tag{5.9}$$

where

$$
\begin{aligned}
\mu_6(\zeta) =& 0.30229989\zeta^3 + 5.0287616 \times 10^{-2}\zeta^4 + 3.6103004 \times 10^{-3}\zeta^5 \\
&+1.0210313 \times 10^{-4}\zeta^6, \\
\theta_5(\zeta) =& 1 + 1.2478566\zeta + 0.55778521\zeta^2 + 0.10432105\zeta^3 \\
&+7.2823921 \times 10^{-3}\zeta^4 + 2.1384429 \times 10^{-4}\zeta^5.
\end{aligned} \tag{5.10}
$$

Baker and Johnson [6] also obtained, by use of

$$X(\zeta) \asymp 2\left(\frac{3\sqrt{\pi}}{4}\right)^{\frac{4}{3}} \zeta^{\frac{4}{3}}, \tag{5.11}$$

and (3.8), the representation,

$$
\begin{aligned}
X(\zeta) &\equiv \hat{X}(z_0(\zeta)) \\
&\approx \zeta^2\frac{\pi}{2}\left[\frac{1 + 0.088412769\zeta}{1 + 0.79551953\zeta + 0.19350034\zeta^2 + 0.013716390\zeta^3}\right]^{\frac{1}{3}},
\end{aligned} \tag{5.12}
$$

We generally use the convention that $F(\zeta) \equiv \hat{F}(z_0(\zeta))$ with $z_0(\zeta)$ explained at (4.9). An exception is the usage $I_n(\zeta) \equiv I_n(z_0(\zeta))$.

The representation of $T(\zeta)$ presents an additional problem not present for the other functions. The asymptotic value as $\zeta \to \infty$ is proportional to ζ, as in the case of Θ, but here we have not been able to evaluate the asymptotic coefficient analytically. This coefficient is the zero temperature diagram evaluated approximately by Monte Carlo by Gell-Mann and Brueckner [15] in their study of the electron-gas correlation energy. We have taken a different approach to its evaluation. We have computed the series through the 31st order and obtain the asymptotic result,

$$\frac{T(\zeta)}{\zeta} \asymp 0.3025 \pm 0.0004, \tag{5.13}$$

where it is the apparent error which we have quoted. This result corresponds to $\epsilon_b^{(2)} = 0.04814 \pm 0.00006$ in the notation of Gell-Mann and Brueckner, in agreement with their result of 0.046 ± 0.002. When we use this asymptotic value, we obtain the representation,

$$T(\zeta) \approx \frac{\nu_6(\zeta)}{\tau_5(\zeta)}, \tag{5.14}$$

where

$$
\begin{aligned}
\nu_6(\zeta) = {} & 1.5397859\zeta^2 + 0.681831\zeta^3 + 0.10939850\zeta^4 \\
& + 8.8741342 \times 10^{-3}\zeta^5 + 2.67165364 \times 10^{-4}\zeta^6 \\
\tau_5(\zeta) = {} & 1 + 1.3317659\zeta + 0.66394907\zeta^2 + 0.15311424\zeta^3 \\
& + 1.6850905 \times 10^{-2}\zeta^4 + 8.8319130 \times 10^{-4}\zeta^5. \qquad (5.15)
\end{aligned}
$$

In addition Baker and Johnson [10] have computed the following representations

$$
z\frac{d}{dz} I_{-\frac{1}{2}}(\zeta) \approx \sqrt{\pi}\zeta \left[\frac{q_9(\zeta)}{r_{13}(\zeta)}\right]^{\frac{1}{3}}, \qquad (5.16)
$$

where

$$
\begin{aligned}
q_9(\zeta) = {} & 1 + 0.37668660\zeta + 9.6301161 \times 10^{-2}\zeta^2 + 1.5693115 \times 10^{-2}\zeta^3 \\
& + 1.9382738 \times 10^{-3}\zeta^4 + 1.7187680 \times 10^{-4}\zeta^5 + 1.1386611 \times 10^{-5}\zeta^6 \\
& + 5.2236572 \times 10^{-7}\zeta^7 + 1.5250645 \times 10^{-8}\zeta^8 + 2.8147079 \times 10^{-10}\zeta^9, \\
r_{13}(\zeta) = {} & 1 + 3.5586672\zeta + 5.6761084\zeta^2 + 5.3449240\zeta^3 + 3.2936668\zeta^4 \\
& + 1.3912374\zeta^5 + 0.41034013\zeta^6 + 8.4619775 \times 10^{-2}\zeta^7 \\
& + 1.2086067 \times 10^{-2}\zeta^8 + 1.1828498 \times 10^{-3}\zeta^9 + 7.9676618 \times 10^{-5}\zeta^{10} \\
& + 3.7403172 \times 10^{-6}\zeta^{11} + 1.1210162 \times 10^{-7}\zeta^{12} \\
& + 2.0835040 \times 10^{-9}\zeta^{13}. \qquad (5.17)
\end{aligned}
$$

$$
z\frac{d}{dz}\Theta(\zeta) \approx \zeta^3 \left[\frac{\sigma_5(\zeta)}{\omega_{13}(\zeta)}\right]^{\frac{1}{3}}, \qquad (5.18)
$$

where

$$
\begin{aligned}
\sigma_5(\zeta) = {} & 0.74589509 + 9.6382201 \times 10^{-2}\zeta + 2.5364237 \times 10^{-2}\zeta^2 \\
& + 1.7998638 \times 10^{-3}\zeta^3 + 1.8272243 \times 10^{-4}\zeta^4 + 6.5777413 \times 10^{-6}\zeta^5, \\
\omega_{13}(\zeta) = {} & 1 + 5.5159030\zeta + 14.121520\zeta^2 + 22.232525\zeta^3 + 24.033724\zeta^4 \\
& + 18.855659\zeta^5 + 11.057783\zeta^6 + 4.9145985\zeta^7 + 1.6582118\zeta^8 \\
& + 0.42040226\zeta^9 + 7.8062423 \times 10^{-2}\zeta^{10} + 1.0090665 \times 10^{-2}\zeta^{11} \\
& + 8.1802486 \times 10^{-4}\zeta^{12} + 3.1641077 \times 10^{-5}\zeta^{13}. \qquad (5.19)
\end{aligned}
$$

$$
z\frac{d}{dz}T(\zeta) \approx \zeta^2 \left[\frac{s_{11}(\zeta)}{t_{16}(\zeta)}\right]^{\frac{1}{3}}, \qquad (5.20)
$$

where

$$
\begin{aligned}
s_{11}(\zeta) = {} & 29.205927 + 18.336679\zeta + 5.7381144\zeta^2 + 1.2777140\zeta^3 \\
& +0.22387177\zeta^4 + 3.1394202 \times 10^{-2}\zeta^5 + 3.4607956 \times 10^{-3}\zeta^6 \\
& +3.3616630 \times 10^{-4}\zeta^7 + 2.2772942 \times 10^{-5}\zeta^8 + 1.4387042 \times 10^{-6}\zeta^9 \\
& +5.0169486 \times 10^{-8}\zeta^{10} + 1.1753523 \times 10^{-9}\zeta^{11}, \\
t_{16}(\zeta) = {} & 1 + 5.6888442\zeta + 15.084824\zeta^2 + 24.728910\zeta^3 + 28.024183\zeta^4 \\
& +23.252756\zeta^5 + 14.592415\zeta^6 + 7.0532994\zeta^7 + 2.6484232\zeta^8 \\
& +0.77327943\zeta^9 + 0.17453022\zeta^{10} \\
& +3.0057345 \times 10^{-2}\zeta^{11} + 3.8682590 \times 10^{-3}\zeta^{12} \\
& +3.6101238 \times 10^{-4}\zeta^{13} + 2.3433749 \times 10^{-5}\zeta^{14} \\
& +9.8914961 \times 10^{-7}\zeta^{15} + 2.2239400 \times 10^{-8}\zeta^{16}.
\end{aligned}
\tag{5.21}
$$

For the e^4 correction to the Debye-Hückel term, we find that for the ion-ion case, we may use the expression for z_{ion} (4.8) in terms of ζ as substituted into (3.52) and (3.54). This yields

$$
-8(0.2842582246 - 0.006578041016)\epsilon^4\zeta^2 Z^2 \left(\frac{m}{M}\right)^{\frac{1}{2}} kT \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}. \tag{5.22}
$$

Similarly, for the electron-ion case, we obtain from (3.59),

$$
-\pi\epsilon^4\zeta Z kT \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \left(\frac{z}{1+z}\right), \tag{5.23}
$$

and we can use the expression (5.1-2) for z.

For the electron-electron case, we need to construct some suitable representations. First, for the case of the $\omega_3 \neq 0$ terms, the series is given by (3.48). In Table 1 we give both the coefficients of the series in z and the corresponding coefficients for the series in ζ. It is to be noticed that substantial cancellation occurs in going from the series in z to that in ζ. We have carried 21 decimal places in the calculation of the fugacity series, and evaluated the integrals to about 18 decimal places using Romberg integration [24] and the Brent multiple precision package [26].

It is helpful to have the asymptotic limit for large z. Since z enters our calculations through Ξ, we need first to compute the limit of Ξ as $z \to \infty$. If we make the change of variables (3.29) and (2.33), but with the electron mass m in (2.33) instead of the ion mass M, then (2.30) becomes,

Table 1
Series coefficients for the $\omega_3 \neq 0$ correction to the Debye Hückel term

n	in fugacity	in de Broglie density
0	0.0000000000 0000000000 E+000	0.0000000000 0000000000 E+000
1	0.0000000000 0000000000 E+000	0.0000000000 0000000000 E+000
2	4.6513774096 5163678750 E−003	4.6513774096 5163678750 E−003
3	−3.4963487161 6090598808 E−003	−2.0732820793 831582707 E−004
4	2.6015308683 2349543112 E−003	9.8879197604 3979831 E−006
5	−2.0076756122 2211161956 E−003	−4.2626300883 636177 E−007
6	1.6028131711 2774032555 E−003	1.5323092299 68351 E−008
7	−1.3152892745 6794096619 E−003	−3.9190088396 787 E-010
8	1.1034163301 7761627824 E−003	1.6080369966 0 E−012
9	−9.4235995629 5790550502 E−004	5.6380750481 E−013
10	8.1671770419 6771805805 E−004	−4.093577309 E−014
11	−7.1655028481 4367263145 E−004	1.70292681 E−015
12	6.3521151009 9370927217 E−004	−3.453999 E−017
13	−5.6811665775 9281693552 E−004	−1.20181 E−018

$$\Xi(\vec{q}, \omega_3) = \frac{4\pi}{(2\pi)^3 kT} \left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}}$$
$$\times \Re \left\{ i \int_0^\infty dt \int_0^K \kappa^2 d\kappa \int_{-1}^1 dx \, \exp\left\{ -t \left[\frac{\omega_3}{kT} + i(2\kappa\nu x - \nu^2) \right] \right\} \right\}, \tag{5.24}$$

where we have used the fact that $n(\vec{k}) = 1$ when $|\vec{\kappa}| \leq K$ and equals zero otherwise in this limit. Doing the integral first over x and then over κ we get

$$\Xi(\vec{q}, \omega_3) = \frac{4}{(2\pi)^2 kT} \left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}}$$
$$\times \Re \left\{ i \int_0^\infty dt \int_0^K \kappa^2 d\kappa \, \exp\left\{ -t \left[\frac{\omega_3}{kT} - i\nu^2) \right] \right\} j_0(2\kappa\nu t) \right\} \tag{5.25}$$
$$= \frac{2K^2}{(2\pi)^2 \nu kT} \left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}} \Re \left\{ i \int_0^\infty \frac{dt}{t} \exp\left[-t \left(\frac{\omega_3}{kT} - i\nu^2 \right) \right] j_1(2K\nu t) \right\},$$

where the $j_n(x)$ are the spherical Bessel functions. Taking the real part (5.25) becomes,

$$\Xi(\vec{q},\omega_3) = -\frac{2\nu K^2}{(2\pi)^2 kT}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty dt\, \exp\left(-t\frac{\omega_3}{kT}\right) j_0(\nu^2 t) j_1(2K\nu t). \tag{5.26}$$

For the case, $\omega_3 = 0$, this integral is a special case of the Weber-Schafheitlin integral and can be done [Gradshteyn and Ryzhik [22], no. 6.574 (1) and (3)]. The result is,

$$\Xi(\vec{q},0) = \begin{cases} -\frac{K}{(2\pi)^2 kT}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}} F\left(1,-\frac{1}{2};\frac{3}{2};\frac{\nu^2}{4K^2}\right), & \text{if } \nu \leq 2\text{K} \\ -\frac{4K^3}{3(2\pi\nu)^2 kT}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}} F\left(1,\frac{1}{2};\frac{5}{2};\frac{4K^2}{\nu^2}\right), & \text{if } \nu > 2\text{K}, \end{cases} \tag{5.27}$$

and

$$\Xi(\vec{0},0) = -\frac{K}{(2\pi)^2 kT}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}}. \tag{5.28}$$

For computational purposes it is worthwhile to note that

$$\begin{aligned} F\left(1,-\frac{1}{2};\frac{3}{2};x^2\right) &= \frac{1}{2} + \frac{1}{4x}(1-x^2)\ln\left(\frac{1+x}{1-x}\right) \quad \text{for } 0 < \text{x} < 1, \\ F\left(1,\frac{1}{2};\frac{5}{2};x^{-2}\right) &= \frac{3}{2}x^2\left[\frac{1}{2x}(1-x^2)\ln\left(\frac{x+1}{x-1}\right)+1\right] \quad \text{for } 1 < \text{x} < \infty \end{aligned} \tag{5.29}$$

By (2.28) the electron-electron contribution from the $\omega_3 = 0$ term is

$$8e^4 kT\left(\frac{2mkT}{\hbar^2}\right)^{-\frac{1}{2}} \int_0^\infty \frac{d\nu}{\nu^2}\left[\Xi(\vec{q},0)^2 - \Xi(\vec{0},0)^2\right] \tag{5.30}$$

If we change variables so that $x = \nu/2K$, then we get the limiting behavior in the large z limit as,

$$\begin{aligned} \frac{4Ke^4}{(2\pi)^4 kT}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{5}{2}} &\left\{\int_0^1 \frac{dx}{x^2}\left[F\left(1,-\frac{1}{2};\frac{3}{2};x^2\right)^2 - 1\right]\right. \\ &\left. + \int_1^\infty \frac{dx}{x^2}\left[\frac{1}{9x^4}F\left(1,\frac{1}{2};\frac{5}{2};x^{-2}\right)^2 - 1\right]\right\}. \end{aligned} \tag{5.31}$$

When we use the asymptotic results,

$$K \asymp [\log z]^{\frac{1}{2}} \quad \text{and} \quad \zeta \asymp \frac{4}{3\sqrt{\pi}} (\log z)^{\frac{3}{2}}, \quad \text{then} \quad K \asymp \left(\frac{3\sqrt{\pi}}{4}\zeta\right)^{\frac{1}{3}}. \tag{5.32}$$

This result allows us to express the large z limit (5.31) as the large ζ limit completely in terms of a quadrature. We have evaluated the integral in (5.31) numerically. The value is -1.644912. We speculate that the exact value is $-\frac{10}{21}\pi\,(3\sqrt{\pi}/4)^{1/3}$. Fortunately these hypergeometric functions have only an $(1-x)\ln(1-x)$ type singularity at $x = 1$.

For the terms from $\omega_3 \neq 0$, we have from (2.28) and (5.26), after performing the sum over ω_3 as we did to obtain (3.45) previously,

$$\frac{32e^4K^4}{(2\pi)^4kT}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{5}{2}} \int_0^\infty d\nu \int_0^\infty dt_1 \int_0^\infty dt_2\, \frac{j_0(\nu^2 t_1) j_1(2K\nu t_1) j_0(\nu^2 t_2) j_1(2K\nu t_2)}{\exp[2\pi(t_1+t_2)]-1}. \tag{5.33}$$

As we are doing the limit as $z \to \infty$, and also (5.32) $K \to \infty$, we will make the change of variables $x = \nu/K$ and $\tau_i = t_i K^2$. Thus (5.33) becomes,

$$\frac{32e^4K}{(2\pi)^4kT}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{5}{2}} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \frac{\int_0^\infty dx\, j_0(x^2\tau_1) j_1(2x\tau_1) j_0(x^2\tau_2) j_1(2x\tau_2)}{\exp\left[2\pi(\tau_1+\tau_2)K^{-2}\right]-1}. \tag{5.34}$$

To proceed further with the analysis of the large z limit, we need to analyze the integral of the four spherical Bessel functions. First, suppose that $\tau_1,\ \tau_2 \ll 1$. Then it will be the large x range which is important, but for small enough τ's, $x\tau_i$ will still be small. Therefore, changing variables so that $y = x^2$, we get by expanding the j_1's,

$$\int_0^\infty dx\, j_0(x^2\tau_1) j_0(x^2\tau_2) j_1(2x\tau_1) j_1(2x\tau_2) \asymp \frac{2\tau_1\tau_2}{9} \int_0^\infty \sqrt{y}dy\, j_0(y\tau_1) j_0(y\tau_2). \tag{5.35}$$

This integral can be done {Gradshteyn and Ryzhik [22] 6.574(1)} and for $\tau_1 \leq \tau_2$ yields,

$$= \frac{\pi\tau_1\tau_2^{\frac{1}{2}}}{9}\sqrt{\frac{2\tau_1}{\pi\tau_2}} F\left[\frac{1}{2}, \frac{1}{4}; \frac{3}{2}; \left(\frac{\tau_1}{\tau_2}\right)^2\right]. \tag{5.36}$$

Thus the integrand of (5.34) is bounded (and of order K^2) at the origin, since $\tau_1 \leq \tau_2$,

$$\frac{\sqrt{\tau_1 \tau_2}}{\tau_1 + \tau_2} \leq \frac{1}{2}, \tag{5.37}$$

for all $\tau_1,\ \tau_2 \geq 0$, and the hypergeometric function is finite over the whole range $0 \leq \tau_1/\tau_2 \leq 1$.

In addition we need to investigate the case $\tau_1,\ \tau_2 \gg 1$. Here the integral over the four Bessel functions in (5.34) reduces to

$$\asymp \int_0^\infty dx\, j_1(2x\tau_1) j_1(2x\tau_2), \tag{5.38}$$

as the range of small x, $x = O(\tau_i^{-1})$, is important here and the j_0 are approximately equal to unity. Again, this integral can be done [Gradshteyn and Ryzhik [22] 6.574 (1)], and yields

$$= \frac{\pi}{12\sqrt{\tau_1 \tau_2}} \left(\frac{\tau_1}{\tau_2}\right)^{\frac{3}{2}}, \tag{5.39}$$

where again we take $\tau_1 \leq \tau_2$. It is of interest to know whether the integrals over the τ's converge for large τ's but yet for $\tau_1 + \tau_2 \ll K^2$. The key quantity to consider is

$$\int_a^\infty d\tau_2 \int_a^{\tau_2} \frac{\tau_1 d\tau_1}{\tau_2^2(\tau_1 + \tau_2)} + \int_a^\infty \int_{\tau_2}^\infty \frac{\tau_2 d\tau_1}{\tau_1^2(\tau_1 + \tau_2)}, \tag{5.40}$$

where a is a sufficiently large lower bound to insure the validity of the asymptotic expression for large τ's that we have derived. Performing the integrations over τ_1 we get,

$$\int_a^\infty \frac{d\tau_2}{\tau_2^2} \left[\tau_2 - a - \tau_2 \ln\left(\frac{2\tau_2}{\tau_2 + a}\right) + \tau_2 - \tau_2 \ln 2\right] \tag{5.41}$$

This integral diverges logarithmically at the upper limit. Thus it is not the case that there is convergence for $\tau_1 + \tau_2 \ll K^2$. Returning to (5.34) we see that in the large K limit, the integral (to leading order) can be treated as if it were cut off for $2\pi(\tau_1 + \tau_2) \approx K^2$. In this case, we see that the leading behavior in (5.41) is just

$$\asymp 4(1 - \ln 2) \ln K. \tag{5.42}$$

Hence, the asymptotic behavior of (5.34) is

$$\frac{8(1-\ln 2)e^4 K^3 \ln K}{3(2\pi)^4 kT}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{5}{2}} \asymp \frac{2\sqrt{\pi}(1-\ln 2)e^4 \zeta \ln \zeta}{3(2\pi)^4 kT}\left(\frac{2mkT}{\hbar^2}\right)^{\frac{5}{2}} \tag{5.43}$$

By means of the results of Table 1, (3.48) and (5.43) we have constructed the following representation for the $\omega_3 \neq 0$ terms. It is

$$\frac{8(1-\ln 2)e^4}{\pi kT}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{5}{2}} \zeta \ln\left[1+\zeta w(\zeta)\right], \tag{5.44}$$

where

$$\begin{aligned} w(\zeta) &= \frac{w_{\mathrm{up}}(\zeta)}{w_{\mathrm{down}}(\zeta)}, \\ w_{\mathrm{up}}(\zeta) &= 0.067346700 + 9.3939016\times 10^{-3}\zeta + 5.4999650\times 10^{-4}\zeta^2 \\ &\quad +1.5556298\times 10^{-5}\zeta^3 + 1.9146773\times 10^{-7}\zeta^4 \\ &\quad +5.1832472\times 10^{-10}\zeta^5, \\ w_{\mathrm{down}}(\zeta) &= 1 + 0.15038586\zeta + 9.9260174\times 10^{-3}\zeta^2 + 3.2718165\times 10^{-4}\zeta^3 \\ &\quad +5.1100023\times 10^{-6}\zeta^4 + 2.5538627\times 10^{-8}\zeta^5. \end{aligned} \tag{5.45}$$

The method used to construct this representation is the method of Padé approximants [11]. There is apparent convergence to within 0.1 percent for $\zeta \leq 64$ and the maximum apparent error for the rest of the range is about 1.4 percent. Owing to the rapid cancellation and the length of time to evaluate the integrals to very high precision, we have not been able to extend the series further in a useful manner. Thus we have not attained here the accuracy of better than 0.1 percent that we have used in all our other representation.

By (3.42), (3.43), (5.31), and (5.32) we have constructed, again by the method of Padé approximants, the following representation, accurate to within 0.1%, for the $\omega_3 = 0$ term. It is,

$$\psi(\zeta) = -\zeta^2\left(\frac{\psi_{\mathrm{up}}(\zeta)}{\psi_{\mathrm{down}}(\zeta)}\right)^{\frac{1}{3}}, \tag{5.46}$$

where

$$\psi_{\mathrm{up}}(\zeta) = 1.0231844 + 0.45318839\zeta + 0.095316231\zeta^2 + 0.011705667\zeta^3$$

$$
\begin{aligned}
&+9.1059919\times 10^{-4}\zeta^4 + 4.2549269\times 10^{-5}\zeta^5 \\
&+1.1069955\times 10^{-6}\zeta^6 \\
\psi_{\mathrm{down}}(\zeta) = {}&1 + 3.5071425\zeta + 5.4925423\zeta^2 + 5.0519900\zeta^3 + 3.0179830\zeta^4 \\
&+1.2217594\zeta^5 + 0.33914784\zeta^6 + 0.063854977\zeta^7 \\
&+7.8956792\times 10^{-3}\zeta^8 + 6.0886249\times 10^{-4}\zeta^9 \\
&+2.7848395\times 10^{-5}\zeta^{10} + 7.2517253\times 10^{-7}\zeta^{11}. \qquad (5.47)
\end{aligned}
$$

In addition we will need representations for the derivatives $z\frac{d}{dz}\ |_{T,\Omega}$ of the $\omega_3 = 0$ and the $\omega_3 \neq 0$ corrections. First, for the $\omega_3 \neq 0$ we have decided to differentiate directly the representation (5.44), in order to maintain thermodynamic consistency in view of the relatively large (up to 1.4 %) error in this representation. Also, it is difficult to construct a suitable form to compute a representation directly from the information at hand. We use the result here that $z\frac{d}{dz} = z\frac{d\zeta}{dz}\frac{d}{d\zeta}$ for our current case. The result is

$$
z\frac{d}{dz}\left\{\zeta \ln[1+\zeta w(\zeta)]\right\} = \zeta\left\{\ln[1+\zeta w(\zeta)] + \frac{\zeta[w(\zeta)+\zeta w'(\zeta)]}{1+\zeta w(\zeta)}\right\}\left[\frac{v_3(\zeta)}{u_5(\zeta)}\right]^{\frac{1}{3}}. \qquad (5.48)
$$

where the $v_3,\ u_5$ are given in (5.7) above.

The representation for $z\frac{d}{dz}\psi$ has been computed by differentiating the series (3.43) and then converting that series into one in ζ by series substitution. We have found it necessary to carry 67 decimal places and to compute 49 terms in the series in order to be sure of adequate convergence. By using the method of Padé approximants, we have derived the following representation,

$$
z\frac{d}{dz}\psi(\zeta) = -\zeta^2\left(\frac{\Psi_{\mathrm{up}}(\zeta)}{\Psi_{\mathrm{down}}(\zeta)}\right)^{\frac{1}{3}}, \qquad (5.49)
$$

which is accurate to within about 0.1%, and where

$$
\begin{aligned}
\Psi_{\mathrm{up}}(\zeta) = {}&8.1854753 + 5.1703568\zeta + 1.6353918\zeta^2 + 0.39395601\zeta^3 \\
&+0.077914611\zeta^4 + 0.012556919\zeta^5 + 1.7216069\times 10^{-3}\zeta^6 \\
&+2.0337199\times 10^{-4}\zeta^7 + 2.0352336\times 10^{-5}\zeta^8 \\
&+1.7240939\times 10^{-6}\zeta^9 + 1.2327804\times 10^{-7}\zeta^{10} \\
&+7.0961694\times 10^{-9}\zeta^{11} + 3.0818831\times 10^{-10}\zeta^{12} \\
&+9.8120219\times 10^{-12}\zeta^{13} + 2.3255188\times 10^{-13}\zeta^{14} \\
&+3.2932567\times 10^{-15}\zeta^{15} + 2.2168101\times 10^{-17}\zeta^{16} \\
\Psi_{\mathrm{down}}(\zeta) = {}&1 + 6.2886448\zeta + 18.642756\zeta^2 + 34.623100\zeta^3 + 45.153698\zeta^4
\end{aligned}
$$

$$
\begin{aligned}
&+43.930225\zeta^5+33.063484\zeta^6+19.701498\zeta^7\\
&+9.4346743\zeta^8+3.6655114\zeta^9+1.1615938\zeta^{10}\\
&+0.30090755\zeta^{11}+0.063692406\zeta^{12}+0.010987487\zeta^{13}\\
&+1.5381071\times10^{-3}\zeta^{14}+1.7373695\times10^{-4}\zeta^{15}\\
&+1.5729005\times10^{-5}\zeta^{16}+1.1322275\times10^{-6}\zeta^{17}\\
&+6.4092767\times10^{-8}\zeta^{18}+2.8021760\times10^{-9}\zeta^{19}\\
&+9.1677492\times10^{-11}\zeta^{20}+2.1198659\times10^{-12}\zeta^{21}\\
&+3.0687902\times10^{-14}\zeta^{22}+2.0529879\times10^{-16}\zeta^{23}
\end{aligned}
\tag{5.50}
$$

In deriving this representation, we have used the result that

$$
z\frac{d}{dz}\psi(\zeta)\asymp\frac{1}{\pi}\left(\frac{4}{3\sqrt{\pi}}\right)^{\frac{1}{3}}\{\mathcal{I}\}\zeta^{-\frac{1}{3}}\approx-0.4761905\zeta^{-\frac{1}{3}}. \tag{5.51}
$$

where $\{\mathcal{I}\}$ is the integral in brackets in (5.31).

6 BEHAVIOR OF THE COEFFICIENTS OF THE PERTURBATION EXPANSION

We show in Fig. 6 the ideal Fermi gas function G_0. In Figs. 7 - 9, we show the ratios of the G_i's to the ideal Fermi gas function. The G_i's are defined by (4.14). These functions are evaluated for the case of aluminum. We have selected aluminum because it is much studied, it is not a complex material, and it is relatively centrally located in the periodic table. It is to be noticed that in the large ζ limit, all these ratios tend to zero, which means that the pressure tends to the ideal gas pressure (for fixed y). In the small ζ limit, the relative size of the coefficients of e^2 and e^4 tends to zero, however that for e^3 remains of order unity. More explicitly, when $\zeta\to0$, The contribution of the G_0 term is a constant, that of the G_2 term is of the order $\zeta^{\frac{2}{3}}y^2$, that of the G_3 is of the order of y^3 and that of the G_4 term is of the order of $\zeta^{\frac{1}{3}}y^4$. In the other limit, $\zeta\to\infty$, the contribution of the G_0 term is of the order of $\zeta^{\frac{2}{3}}$, that of the G_2 term is of the order of y^2, that of the G_3 term is of the order of y^3, and that of the G_4 term is of the order of $\zeta^{\frac{1}{3}}y^4$. The G_4 term requires some additional comment. The ion-ion correction term to the Debye-Hückel term becomes dominant in G_4 (4.18) for very large ζ. Remember that we are only treating the ions as Maxwell Boltzmann particles, that we are ignoring ion-ion exchange, and most fundamental, that we are treating m/M as negligibly small. In this region, a better treatment of the ions is surely required not only for the ion-ion terms but also for the electron-ion terms as well. As long as these terms are small, we feel the treatment is adequate, but the treatment is probably insufficient when they become dominate.

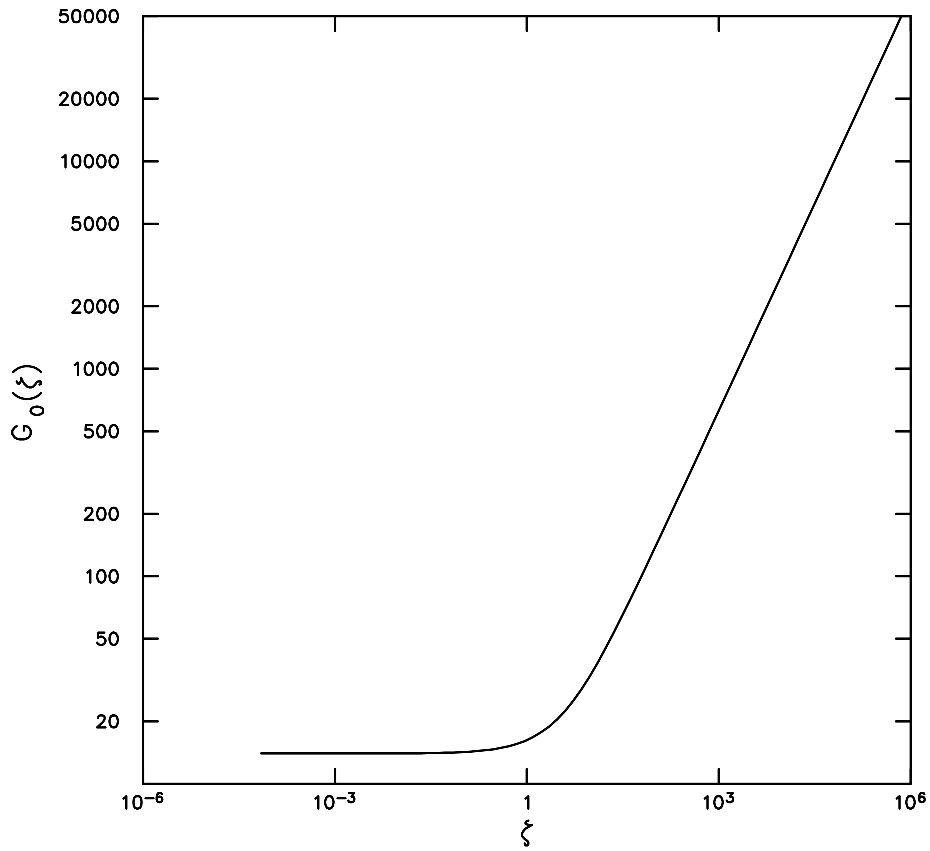

Fig. 6. The Fermi ideal gas function times Z, plus 1, which is the value of $p\Omega/NkT$ in the absence of Coulomb interactions.

A fuller comparison of the size of the corrections to the ideal gas has been made. In order to gain some indication of the region of validity of the expansion we have computed the values of $y(\zeta)$ for which the third order (most restrictive) and the fourth order terms are equal to 0.1%, 1.0% and 10.0% of the value of the ideal gas function. These results are plotted in figures 10 and 11, again for the case of aluminum. The regions above the plotted curves correspond to smaller values of y.

In Fig. 10 we have also plotted the extrapolation of the Lindemann law for the melting curve assuming that the Grüneisen constant $\gamma = \frac{2}{3}$. This curve is provided for orientation, relative to our expansion results. One obvious feature seen in Fig. 10 is the strong cusps in the error contours along a line of constant ζ. The explanation for this feature can be seen in Fig. 9 and corresponds to the value of ζ for which $G_4(\zeta) = 0$. At this point, the corresponding $y \to \infty$, which causes the cusp.

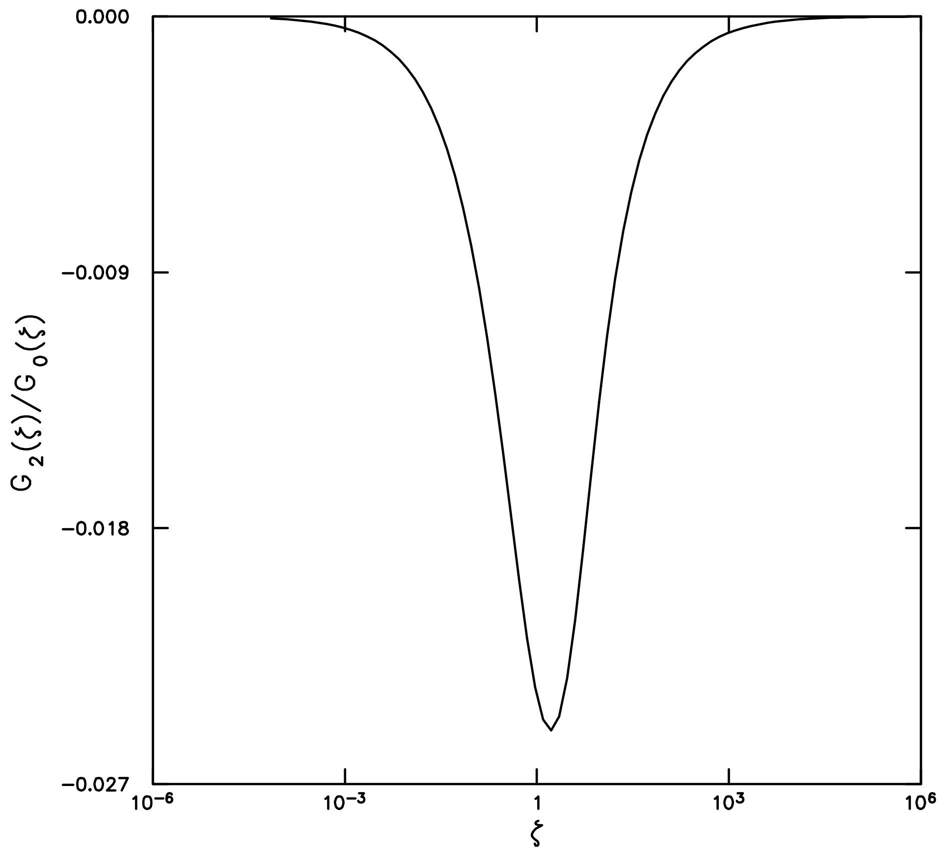

Fig. 7. The ratio of the coefficient of y^2 to the ideal gas function.

In Fig. 11, we see that the region of validity of the ideal gas formula extends to lower temperature as the density increases. For densities higher than those plotted the approximations that we have used which treat m/M as neglectably small ($\frac{m}{M} \approx 2.0338 \times 10^{-5}$ for aluminum) may break down. One example would be the attractive electron-ion term for $\omega_3 \neq 0$ (3.57) which we have omitted. There are a number of other effects that come into play as the density increases.

7 LOW DENSITY IONIZATION PROFILE

The results of the previous section allow us to give the leading order terms in the expansion in inverse temperature of the terms of the low density expansion of the pressure. We complete the results of (4.17) of ref.[9]. Thus we have,

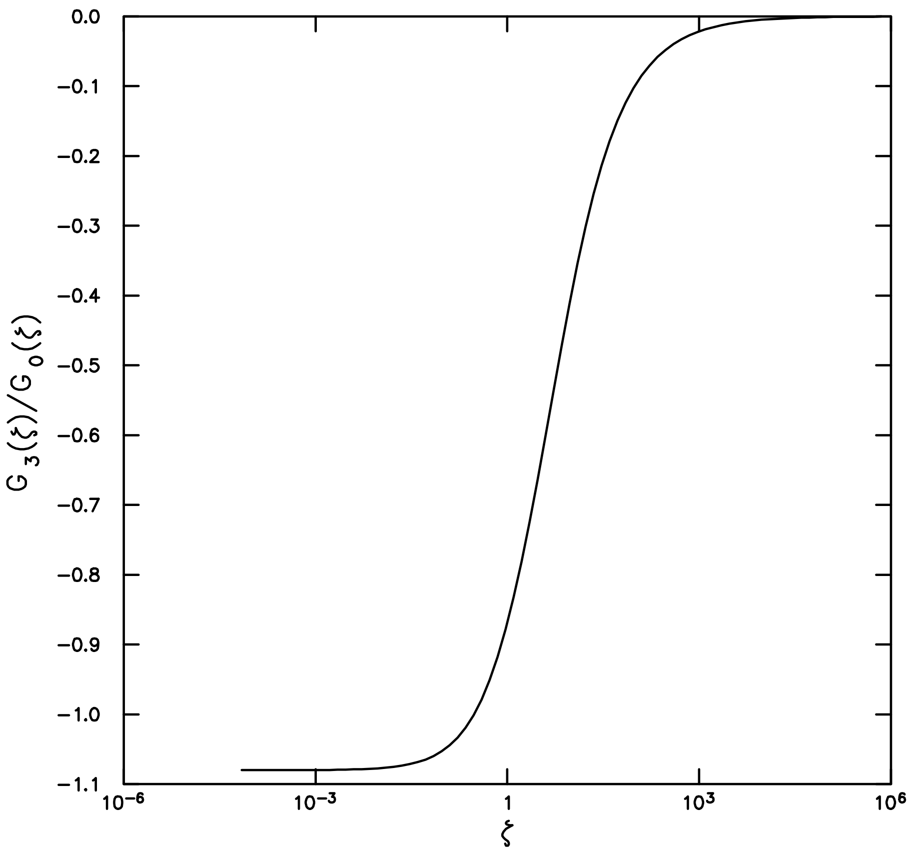

Fig. 8. The ratio of the coefficient of y^3 to the ideal gas function.

$$\frac{p\Omega}{NkT} = 1 + Z\Bigg\{1 - \zeta^{\frac{1}{2}}\left[\frac{\sqrt{2\pi}}{3}(Z+1)^{\frac{3}{2}}\epsilon^3 + \ldots\right]$$
$$+\zeta\left[\frac{1}{2^{\frac{5}{2}}} - \frac{1}{2}\epsilon^2 + \left(\frac{\pi\ln 2}{2\sqrt{2}} + \frac{\pi\sqrt{2}}{4} - \frac{\pi}{2}Z - \frac{\pi\sqrt{2}}{4}Z^2\left(\frac{m}{M}\right)^{\frac{1}{2}}\right)\epsilon^4 + \ldots\right]$$
$$+\zeta^{\frac{3}{2}}\left[\frac{3\sqrt{\pi}}{2}(Z+1)^{\frac{1}{2}}\epsilon^3 + \ldots\right] + o\left(\zeta^{\frac{3}{2}}\right)\Bigg\}, \qquad (7.1)$$

where ϵ is given by (4.5). We have compared this result with those of DeWitt *et al.*[27] and find agreement in this limit, except for the $\zeta^{\frac{3}{2}}$ term where their result appears to be too large by a factor of 2. Note that their result is only for an electron gas, so the ion-ion terms (which are dominant in the coefficients of ϵ^3 and ϵ^4 for large ζ) do not appear in their results.

One of the conclusions which can be drawn from (7.1) is the low density limit of the ionization profile, at least for high temperatures. Since in Saha theory [28] it is common to take the degree of ionization to be proportional to the

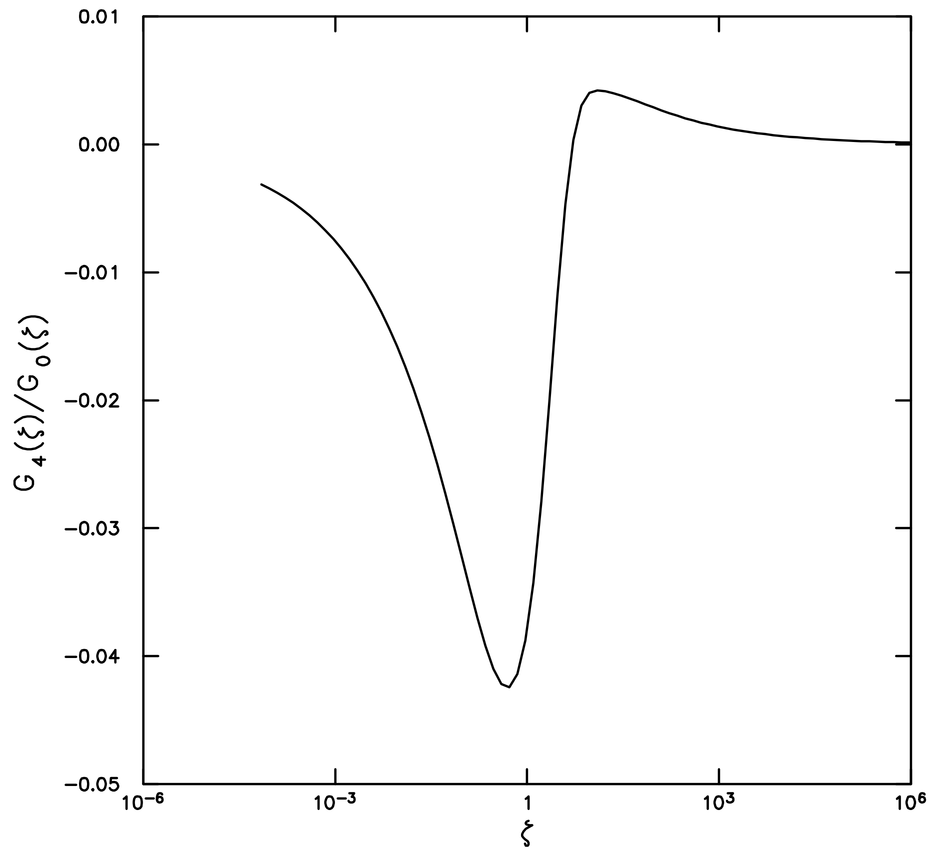

Fig. 9. The ratio of the coefficient of y^4 to the ideal gas function.

electron pressure, dividing the electron pressure by the ideal electron pressure, we deduce,

$$\lim_{r_b \to \infty} \frac{1 - \frac{Z_i}{Z}}{\left[(Z+1)\,\frac{a_0}{r_b}\right]^{\frac{3}{2}}} = \sqrt{\frac{2}{3}Z}\left(\frac{13.6052}{T_{\mathrm{ev}}}\right)^{\frac{3}{2}}, \tag{7.2}$$

where a_0 is the Bohr radius. By contrast, the Saha formula [28]

$$\frac{Z_i}{Z} = \frac{1}{1 + A\zeta \exp(\chi/T)} \tag{7.3}$$

gives

$$1 - \frac{Z_i}{Z} \propto \frac{\rho}{T^{\frac{3}{2}}}, \quad \text{instead of} \quad \propto \frac{\rho^{\frac{1}{2}}}{T^{\frac{3}{2}}}, \tag{7.4}$$

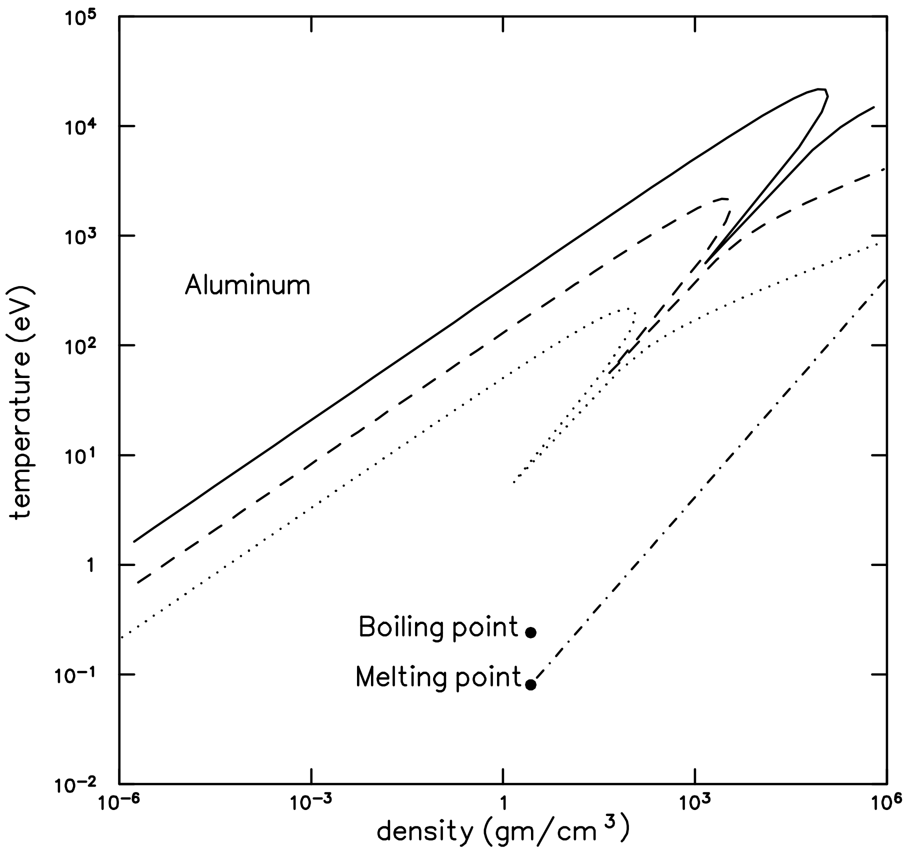

Fig. 10. The contours where the $G_4(\zeta)y^4$ term contributes 0.1% (solid curve), 1% (dashed curve) and 10% (dotted curve) of the ideal gas pressure. The dashed-dotted curve is the extrapolated value of the melting curve according to the Lindemann law, assuming the Grüneisen constant $\gamma = \frac{2}{3}$.

given by (7.2). Here ρ is the electron density. The difference in the power of ρ is presumably a combination of quantum and Coulomb effects.

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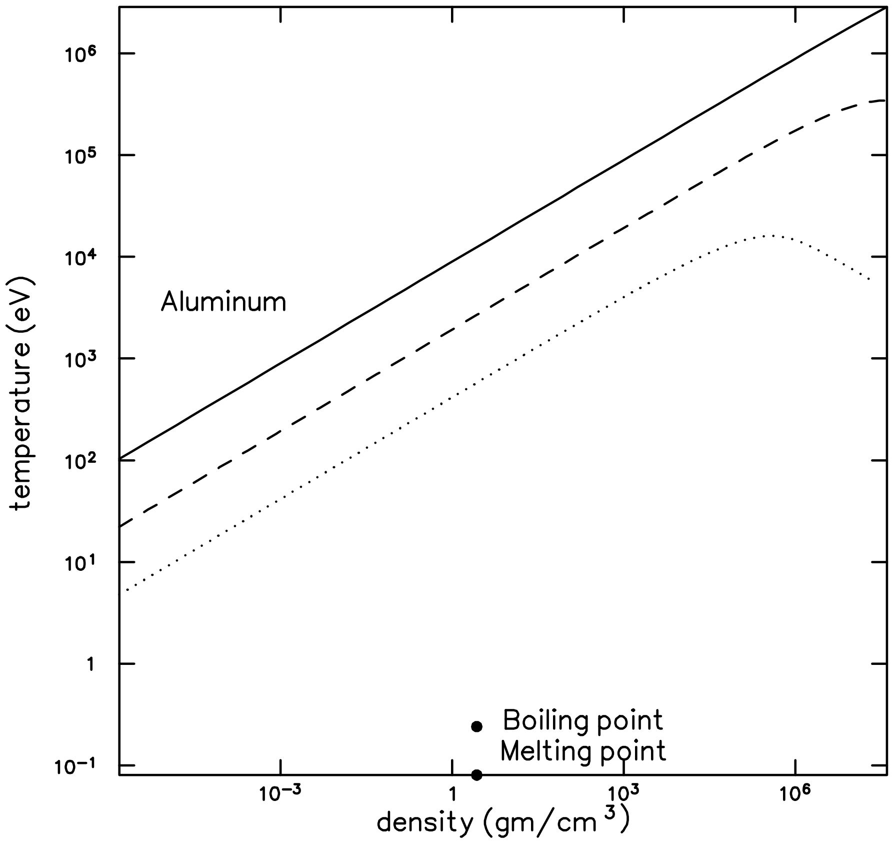

Fig. 11. The contours where the $G_3(\zeta)y^3$ term contributes 0.1% (solid curve), 1% (dashed curve) and 10% (dotted curve) of the ideal gas pressure.

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